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SYNTHESIS OF *C*-GLYCOSYL COMPOUNDS BY THE WITTIG IODOCYCLIZATION PROCEDURE. DIFFERENCES FROM MERCURIOCYCLIZATION

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ABSTRACT

Various sugars were *C*-glycosylated by treatment with methylenetriphenylphosphorane and subsequent iodocyclization of the resulting hept- and hex-enitols. In all cases, a *C*-glycofuranosyl compound was obtained, except for 3,4,5,7-tetra-*O*-benzyl-1,2-dideoxy-D-*manno*-hept-1-enitol which yielded a *C*-pyranosyl compound. High stereoselection, with formation of the 1,2-*cis* adduct as major product, was observed when an asymmetric center was present in the position adjacent to the double bond.

INTRODUCTION

C-Glycosyl compounds have recently gained interest as building blocks for the synthesis of a large number of natural products[1] and as potential inhibitors of metabolic processes[2–8]. A two-step procedure to obtain the *C*-glycosyl compounds 3, first employed by Orhui *et al.*[9], involves the formation of an unsaturated, open-chain derivative 2, followed by cyclization. For the first step, stabilized Wittig reagents[9–11] or methylenetriphenylphosphorane[4–7,12,13] have been employed. The subsequent cyclization of the unsaturated derivative 2 may occur through a Michael reaction by treatment with bases or, sometimes spontaneously, when stabilized ylids are employed; a mixture of the two anomers is generally formed†. In 1981, Pougny *et al.*[12] introduced activation of the double bond with an electrophile, which represents a more general procedure and, in addition, allows better stereocontrol[7,15–17]. Our recent studies[13] on the stereochemistry of the mercuriocyclization of some polybenzylated enitols have shown that the stereochemical course of the reaction is largely dependent on the configuration at the carbon atom adjacent to the carbonyl group of the starting sugar. We report herein our results on the iodocyclization of some hept- and hex-enitols, which differ to some extent from those obtained in the

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†For some exceptions, see ref. 11 and 14.

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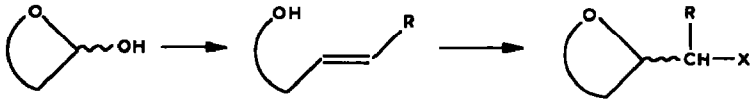


1 2 3

mercury-promoted ring closure.

RESULTS AND DISCUSSION

The Wittig reactions took place at room temperature in oxolane-N,N,N′,N′,N″,N″-hexamethylphosphoric triamide [$(CH_2)_4O$-$(Me_2N)_3PO$] by adding a solution of the sugar (1 equiv.) to the ylid prepared from methyltriphenylphosphonium iodide (5 equiv.) and 1.6M butyllithium in hexane (5 equiv.), under a dry nitrogen atmosphere. The presence of $(Me_2N)_3PO$, in some cases, enchanced the rate of the reaction (**6**, Table I) and allowed better yields (**6**, **9**, and **12**). However, with 2,3,4,6-tetra-*O*-benzyl-D-glucose, the above-mentioned conditions led to an elimination reaction, affording 3,5,7-tri-*O*-benzyl-1,2,4-trideoxy-D-*erythro*-hepta-1,3-dienitol (**5**) in 80% yield. The desired 3,4,5,7-tetra-*O*-benzyl-1,2-deoxy-D-*gluco*-hept-1-enitol (**4**) could be obtained in 54% yield with the procedure previously described[13].

First of all, we performed the iodocyclization on the glucopheptenitol **4**; under Barlett *et al.*[18] cynetic conditions (iodine, sodium hydrogencarbonate, and acetonitrile) or with *N*-iodosuccinimide, the double bond was unreactive*, whereas, under

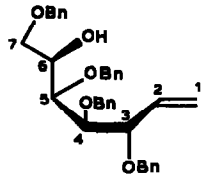
TABLE I

SYNTHESIS OF HEPT- AND HEX-ENITOLS BY WITTIG REACTION WITH METHYLENETRIPHENYLPHOSPHORANE.

Compound formed	*Solvent*	*Ylid (equiv.)*	*Conditions*[a]		*Yield %*
			Temp.[a]	*Time (h)*	
4[b]	$(CH_2)_4O$	2	R.t.,	24	54
5	$(CH_2)_4O$-$(Me_2N)_3PO$	5	R.t.,	18	79
6[b]	$(CH_2)_4O$	2	Reflux,	3	24
6	$(CH_2)_4O$-$(Me_2N)_3PO$	5	R.t.,	2.5	27
7	$(CH_2)_4O$-$(Me_2N)_3PO$	5	R.t.,	1.5	70
9[b]	$(CH_2)_4O$	5	R.t.	3	10
9	$(CH_2)_4O$-$(Me_2N)_3PO$	5	R.t.,	3	41
10 and 11	$(CH_2)_4O$-$(Me_2N)_3PO$	5	R.t.,	3	45
12[b]	$(CH_2)_4O$	3.5	R.t.,	2.5	21
12	$(CH_2)_4O$-$(Me_2N)_3PO$	5	R.t.,	3	59

[a]R.t., room temperature. [b]Ref. 13.

*This double bond also showed no reactivity towards several epoxidizing reagents, such as 3-chloroperoxybenzoic acid, hydrogen peroxide–acetonitrile, and trifluoroperoxyacetic acid.



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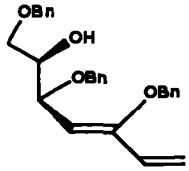

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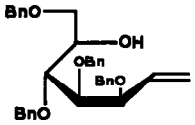

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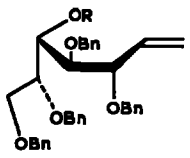
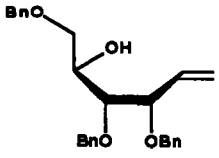


7 R = H
8 R = Bn



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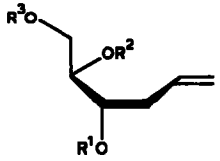


10 $R^1 = R^3 = Bn, R^2 = H$
11 $R^1 = R^2 = Bn, R^3 = H$
12 $R^1 = R^2 = H, R^3 = Tr$

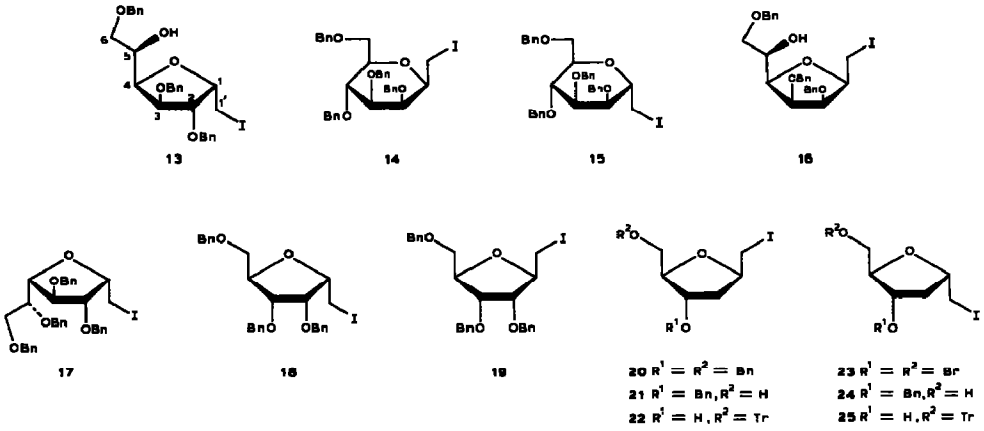
slightly acidic conditions[19] (pH 4, oxolane–water), the compound underwent ring closure to give the *C*-furanosyl derivative **13** (Table II) with concomitant debenzylation at O-5. When other hex- and hept-enitols were subjected to the last-mentioned acidic conditions, in almost all the cases the adduct was a *C*-furanosyl compound, the only exception being the D-*manno*-heptenitol **6** (Table II). When an asymmetric carbon atom was present at the allylic position (**4**, **6**, **7**, **8**, and **9**; Table II), the reaction showed a high stereoselection, always yielding the 1,2-*cis* adduct as the major or sole product. When the allylic position was unsubstituted, (**10**, **11**, and **12**; Table II), almost the same amount of the two anomers was obtained.

TABLE II

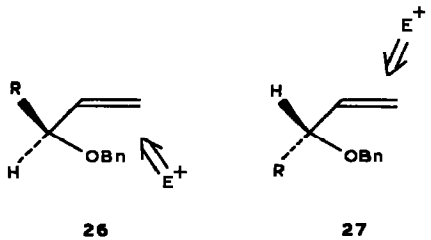
REACTION OF HEPT- AND HEX-ENITOLS WITH IODINE[a]

Starting compound	*Resulting compound(s)*	*Ratio*	*Yield (%)*
4	**13**		75
6	**14** and **15**	41:9 (β:α)	42
7	**17**		70
8	**17**		78
9	**18** and **19**	17:3 (α:β)	67
10	**20** and **23**	13:7 (β:α)	72
11	**21** and **24**	21:29 (β:α)	50
12	**22** and **25**	49:51 (β:α)	55

[a]Three equivalents of iodine in oxolane–water at pH 4.



From a stereochemical point of view, these results are analogous to those obtained when a mercury salt was utilized as promoter of the cyclization; the stereochemistry of the addition of the electrophile showed to be the same, a 1,2-*cis* relationship being obtained in both cases. The stereochemical results may be explained by assuming that the reactive conformations of the enitols are **26** and **27**, in which the allylic oxygen atom lies on about the same plane as that of the double bond, and the electrophile approaches the molecule from the less hindered side.



On the contrary, iodocyclization is quite different from mercuriocyclization with respect to the ring-size of the adducts obtained. Whereas, in the latter case, the free hydroxyl group is the only nucleophile that can promote the internal substitution on the intermediate cation, in the former case, either the hydroxyl or the benzyloxy group can cyclize to yield, in all the cases but one, a furanosyl derivative. The formation of five-membered rings is always preferred over that of six-membered rings; the only exception observed, the formation of a pyranosyl compound from the D-*manno*-heptenitol **6**, may be explained by the overcrowding of a transition state which yields a tetrasubstituted-oxolane ring (**16**) with three 1,2-*cis* interactions[20]. The difference between the factors that determine the ring-size during the closure can be exploited in order to obtain, from the same enitol, either a *C*-glycopyranosyl or a *C*-glycofuranosyl compound only by choosing the proper electrophile; for example, compound **4** gave by treatment with mercury(II) acetate[12] and

iodine, respectively, a six-membered[13] and a five-membered ring. So iodocyclization and mercuriocyclization can become complemental in control of the ring-size.

EXPERIMENTAL

General methods. — Optical rotations were measured with a Perkin–Elmer 241 polarimeter. Analytical t.l.c. was carried out on Merck 60 F_{254} Silica gel plates (0.25-mm layer thickness) and the spots were detected either by a u.v. lamp or by spraying with 50% aqueous H_2SO_4 and heating at 110° for 5 min. Column chromatography was performed with Merck 60 Silica gel (70–230 mesh) and elution with mixtures of hexane–ethyl acetate of various compositions. ^{1}H-N.m.r. spectra were recorded with a Brüker WP-80 or with a Varian XL-200 spectrometer, and ^{13}C-n.m.r. spectra with a Varian XL-100 spectrometer for solutions in $CDCl_3$ containing tetramethylsilane as an internal standard. "Processing" refers to dilution with water, extraction with an organic solvent, washing to neutrality, drying (Na_2SO_4), filtration, and evaporation under reduced pressure.

*(2,3,6-Tri-*O*-benzyl-α-*D*-glucofuranosyl)iodomethane* (**13**). — 3,4,5,7-Tetra-*O*-benzyl-1,2,-dideoxy-D-*gluco*-hept-1-enitol[13] (**4**; 114 mg, 0.21 mmol) was dissolved in oxolane (0.2 mL) and 0.5M (pH 4.0) phtalate buffer (1 mL) was added. A solution of I_2 (161 mg, 0.63 mmol) in oxolane (0.8 mL) was slowly added to the rapidly stirred mixture. After 1 h, the excess of I_2 was eliminated with aqueous Na_2SO_3 and processing afforded a crude product that was chromatographed to yield **13** (91 mg, 75%), oil, $[\alpha]_D^{20}$ −33° (*c* 1.0, chloroform); ^{1}H-n.m.r. (200 MHz): δ 2.6 (bd, 1 H, *J*4 Hz, OH), 3.21 and 3.31 (2 H, AB part of an ABX system, $J_{1'a,1'b}$ 9.5, $J_{1'a,1}$ 5.5, and $J_{1'b,1}$ 10 Hz, CH_2I), 3.4–3.8 (m, 2 H, H-6a, 6b), 4.0–4.2 (m, 4 H, H-2,3,4,5), 4.43 (ddd, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.5–4.6 (m, 6 H, CH_2Ph), and 7.2–7.4 (m, 15 H, Ph); ^{13}C-n.m.r. (100 MHz) δ: 1.2 (CH_2I).

Anal. Calc. for $C_{28}H_{31}IO_5$: C, 58.54; H, 5.44. Found: C, 58.14; H, 5.56.

*3,4,5,7-Tetra-*O*-benzyl-1,2-dideoxy-*D*-manno-hept-1-enitol* (**6**). — A 1.6M hexane solution of butyllitium (8.47 mL, 13.6 mmol) was slowly added to a solution of methyltriphenylphosphonium iodide (5.84 g, 13.6 mmol) in dry oxolane (17 mL) under N_2; dry $(Me_2N)_3PO$ (2.4 mL) was then added, followed by the slow addition of a solution of 2,3,4,6-tetra-*O*-benzyl-D-mannopyranose (1.46 g, 0.271 mmol) in oxolane (5.4 mL) and $(Me_2N)_3PO$ (7.2 mL). After 2.5 h, a saturated aqueous solution of NH_4Cl was added, followed by processing. The crude product was submitted to column chromatography to yield **6** (394 mg, 27%).

Anal. Calc. for $C_{35}H_{38}O_5$: C, 78.04; H, 7.11. Found: C, 77.70; H, 6.99.

*(2,3,4,6-Tetra-*O*-benzyl-β-*D*-mannopyranosyl)iodomethane* (**14**) *and (2,3,4,6-tetra-*O*-benzyl-α-*D*-mannopyranosyl)iodomethane* (**15**). — 3,4,5,7-Tetra-*O*-benzyl-1,2-dideoxy-D-*manno*-hept-1-enitol (**6**) (120 mg, 0.22 mmol) was iodocyclized according to the aforementioned procedure for 3 h. Processing afforded a crude product (110 mg) which was chromatographed on a silica gel column. The main product (63 mg, 42%) was obtained as a mixture of the β- and α- anomer (**14** and **15**)

in a 41:9 ratio. They were separated by careful chromatography on silica gel in 99:1 benzene–ethyl acetate.

Compound **14**. $[\alpha]_D^{20}$ −2° (*c* 1.1, chloroform); ^{1}H-n.m.r. (200 MHz): δ 3.30 (d, 2 H, *J* 7 Hz, CH_2I), 3.49 (ddd, 1 H, $J_{5,6a}$ 2, $J_{5,6b}$ 5.5, and $J_{4,5}$ 9.5 Hz, H-5), 3.55 (dt, 1 H, $J_{1,2}$ 1 Hz, H-1), 3.63 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 9.5 Hz, H-3), 3.67 and 3.77 (2 H, AB part of an ABX system, $J_{6a,6b}$ 11 Hz, H-6a,6b), 3.91 (t, 1 H, *J* 9.5 Hz, H-4), 4.21 (dd, 1 H, H-2), 4.5–5.1 (8 H, m, C*H*$_2$Ph), and 7.1–7.4 (m, 20 H, Ph); ^{13}C-n.m.r. (100 MHz): δ 3.2 (CH_2I).

Anal. Calc. for $C_{35}H_{37}IO_5$: C, 63.26; H, 5.61. Found: C, 63.33; H, 5.50.

Compound **15**. $[\alpha]_D^{20}$ +11° (*c* 0.9, chloroform); ^{1}H-n.m.r. (200 MHz): δ 3.34 and 3.41 (2 H, AB part of an ABX system, $J_{1'a,1'b}$ 10.5, $J_{1'a,1}$ 5.5 $J_{1'b,1}$ 4 Hz), 3.6–4.4 (m, 7 H, H-1,2,3,4,5,6a,6b), 4.4–4.6 (m, 8 H, C*H*$_2$Ph), and 7.1–7.4 (m, 20 H, Ph); ^{13}C- (100 MHz): δ 7.0 (CH_2I).

Anal. Calc. for $C_{35}H_{37}IO_5$: C, 63.26; H, 5.61. Found: C, 63.01; H, 5.42.

*3,4,6,7-Tetra-*O*-benzyl-1,2-dideoxy-*D-galacto-*hept-1-enitol* (**7**). — 2,3,5,6-Tetra-*O*-benzyl-D-galactofuranose (1.22 g, 0.226 mmol) was subjected to the Wittig reaction according to the aforementioned conditions for 1.5 h. Column chromatography of the crude product yielded **7** (851 mg, 70%), oil, $[\alpha]_D^{20}$ −20° (*c* 1.1, chloroform); ^{1}H-n.m.r. (80 MHz): δ 2.97 (d, 1 H, *J* 6.5 Hz, OH), 3.5–4.0 (m, 5 H, H-4,5,6,7a,7b), 4.20 (ddt, 1 H, $J_{2,3}$ 7, $J_{3,4}$ 3, $J_{3,1a}$, $J_{3,1b}$ 1 Hz, H-3), 4.3–4.9 (m, 8 H, C*H*$_2$Ph), 5.31 and 5.33 (2 H, AB part of an ABMXY system, $J_{1a,1b}$ 2.5, $J_{1a,2}$ 10, $J_{1b,2}$ 18 Hz, H-1a,1b), 6.02 (ddd, 1 H, H-2), and 7.1–7.4 (m, 20 H, Ph).

Anal. Calc. for $C_{35}H_{38}O_5$: C, 78.04; H, 7.11. Found: C, 78.29; H, 7.03.

*3,4,5,6,7-Penta-*O*-benzyl-1,2-dideoxy-*D-galacto-*hept-1-enitol* (**8**). — NaH (55%, oil dispersion; 49 mg, 1.12 mmol) was washed three times with dry ethyl ether and dissolved into *N,N*-dimethylformamide (1.3 mL) under N_2. Compound **7** (404 mg, 0.75 mmol), dissolved in *N,N*-dimethylformamide (1 mL), was added and the mixture stirred for 1 h at room temperature and 1 h at 50°. The solution was cooled to room temperature and benzyl bromide (0.11 mL, 0.92 mmol) added. After 18 h, a saturated solution of NH_4Cl was added and the crude product obtained after processing was chromatographed on silica gel and eluted with 99:1 benzene–ethyl acetate to yield 3,5,6,7-tetra-*O*-benzyl-1,2,4-trideoxy-D-*threo*-hepta-1,3-dienitol (90 mg, 23%) and **8** (206 mg, 44%), $[\alpha]_D^{20}$ +4° (*c* 1.1, chloroform); ^{1}H-n.m.r. (80 MHz): δ 3.6–4.0 (m, 5 H, H-4,5,6,7a,7b), 4.12 (ddt, 1 H, $J_{2,3}$ 7.5, $J_{3,4}$ 3, $J_{3,1a}$, $J_{3,1b}$ 1 Hz, H-3), 4.3–4.9 (m, 10 H, C*H*$_2$Ph), 5.24 and 5.31 (2 H, AB part of an ABMXY system, $J_{1a,1b}$ 2.5, $J_{1a,2}$ 10, $J_{1b,2}$ 17.5 Hz, H-1a,1b), 5.97 (ddd, 1 H, H-2), and 7.1–7.5 m, 25 H, Ph).

Anal. Calc. for $C_{42}H_{44}O_5$: C, 80.23; H, 7.05. Found: C, 79.85; H, 6.90.

*(2,3,5,6-Tetra-*O*-benzyl-α-*D-*galactofuranosyl)iodomethane* (**17**). — (*a*) *From* **7**. Compound **7** (112 mg, 0.21 mmol) was iodocyclized according the usual procedure for 40 min to yield, after chromatography, **17** (97 mg, 70%), oil, $[\alpha]_D^{20}$ −39° (*c* 1.0, chloroform); ^{1}H-n.m.r. (200 MHz): δ 3.29 and 3.34 (2 H, AB part of an ABX system, $J_{1'a,1'b}$ 9.5, $J_{1'a,1}$ 6.5, $J_{1'b,1}$ 8 Hz, CH_2I), 3.56 and 3.63 (2 H, AB part of an

ABX system, $J_{6a,6b}$ 10, $J_{6a,5}$ 6, $J_{6b,5}$ 4 Hz, H-6a,6b), 3.77 (ddd, 1 H, $J_{4,5}$ 5.5 Hz, H-5), 4.01 (dd, 1 H, $J_{1,2}$ 4, $J_{2,3}$ 0.5 Hz, H-2), 4.06 (dd, 1 H, $J_{3,4}$ 3.5, H-3), 4.13 (dd, 1 H, H-4), 4.26 (ddd, 1 H, H-1), 4.35–4.8 (m, 8 H, CH_2Ph), and 7.1–7.4 (m, 20 H, Ph); ^{13}C-n.m.r. (100 mHz): δ 0.5 (CH_2I).

Anal. Calc. for $C_{35}H_{37}IO_5$: C, 63.26; H, 5.61. Found: C, 62.85; H, 5.70.

(*b*) *From* **8**. Compound **8** (53 mg, 84 μmol) was iodocyclized according to the usual procedure for 40 min to yield a compound (47 mg, 78%) indistinguishable from **17**, described under (*a*).

(2,3,5-Tri-O-benzyl-α-D-ribofuranosyl)iodomethane (**18**) *and (2,3,5-tri-O-benzyl-β-D-ribofuranosyl)iodomethane* (**19**). — 3,4,6-Tri-*O*-benzyl-1,2,-dideoxy-D-*ribo*-hex-1-enitol (**9**) (107 mg, 0.256 mmol) was iodocylcized (reaction time; 1 h) to yield, after column chromatography, **18** (79 mg) and **19** (14 mg) (67% overall yield).

Compound **18**. $[\alpha]_D^{20}$ +13° (*c* 1.0, chloroform); ^{1}H-n.m.r. (200 MHz); δ 3.33 and 3.44 (2 H, AB part of an ABX system, $J_{1'a,1'b}$ 9.5, $J_{1'a,1}$ 6.5, $J_{1'b,1}$ 8 Hz, CH_2I), 3.49 and 3.61 (2 H, AB part of an ABX system, $J_{5a,5b}$ 11, $J_{5a,4}$ 4, $J_{5b,4}$ 3 Hz, H-5a,5b), 4.10 (dd, 1 H, $J_{2,3}$ 4, $J_{3,4}$ 7 Hz, H-3), 4.20 (t, 1 H, *J* 4 Hz, H-2), 4.26 (ddd, 1 H, H-4), 4.32 (ddd, 1 H, H-1), 4.4–4.9 (m, 6 H, CH_2Ph), and 7.1–7.4 (m, 15 H, Ph); ^{13}C-n.m.r. (100 MHz): δ 3.6 (CH_2I).

Anal. Calc. for $C_{27}H_{29}IO_4$: C, 59.57; H, 5.37. Found: C, 59.62; H, 4.98.

Compound **19**. $[\alpha]_D^{20}$ −6° (*c* 0.5, chloroform); ^{1}H-n.m.r. (200 MHz): δ 3.24 and 3.29 (2 H, AB part of an ABX system, $J_{1'a,1'b}$ 10.5, $J_{1'a,1}$ 5, $J_{1'b,1}$ 5 Hz, CH_2I), 3.52 (d, 2 H, *J* 4.5 Hz, H-5a,5b), 3.75 (t, 1 H, *J* 5 Hz, H-3 or -2), 3.94 (t, 1 H, *J* 5 Hz, H-2 or -3), 3.95 (q, 1 H, *J* 5 Hz, H-4 or -1), 4.25 (q, 1 H, H-1 or -4), 4.4–4.7 (m, 6 H, CH_2Ph), and 7.1–7.4 (m, 15 Hz, Ph); ^{13}C-n.m.r. (100 MHz): δ 7.8 (CH_2I).

Anal. Calc. for $C_{27}H_{29}IO_4$: C, 59.57; H, 5.37. Found: C, 59.70; H, 5.20.

*4,6-Di-O-benzyl-1,2,3-trideoxy-*D-erythro-*hex-1-enitol* (**10**) *and 4,5-di-O-benzyl-1,2,3-trideoxy-*D-erythro-*hex-1-enitol* (**11**). — A 1:2 mixture (700 mg) of 3,5-di-*O*-benzyl-2-deoxy-D-*erythro*-pentose and 3,4-di-*O*-benzyl-2-deoxy-D-*erythro*-pentose were treated with methylenetriphenylphosphorane under the conditions just described for 3 h to yield after chromatography, **10** (104 mg) and **11** (209 mg) (45% overall yield).

Compound **10**. $[\alpha]_D^{20}$ +25° (*c* 1.0, chloroform); ^{1}H-n.m.r. (80 MHz): δ 2.36 (d, 1 H, *J* 4.5 Hz, OH), 2.42 (bt, 2 H, *J* 7 Hz, H-3), 3.4–3.7 (m, 3 H, H-4,6a,6b), 4.88 (m, 1 H, H-5), 4.4–4.8 (m, 4 H, CH_2Ph), 5.0–5.3 (m, 2 H, H-1a,1b), 5.92 (ddt, 1 H, $J_{2,3}$ 7, $J_{1a,2}$ 10, $J_{1b,2}$ 17 Hz, H-2), and 7.1–7.4 (m, 10 H, Ph).

Anal. Calc. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 77.03; H, 7.61.

Compound **11**. $[\alpha]_D^{20}$ +7° (*c* 0.8, chloroform); ^{1}H-n.m.r. (80 MHz): δ 2.18 (bt, 1 H, *J* 6 Hz, OH), 2.44 (bt, 2 H, *J* 6.5 Hz, H-3), 3.4–3.9 (m, 4 H, H-4,5,6a,6b), 4.4–4.8 (m, 4 H, CH_2Ph), 5.0–5.3 (m, 2 H, H-1a,1b), 5.87 (ddt, 1 H, $J_{2,3}$,7 $J_{1a,2}$ 9.5, $J_{1b,2}$ 17 Hz, H-2), and 7.1–7.4 (m, 10 H, Ph).

Anal. Calc. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.90; H, 7.40.

*(3,5-Di-O-benzyl-2-deoxy-β-D-*erythro-*pentofuranosyl)iodomethane* (**20**) *and (3,5-di-O-benzyl-2-deoxy-α-D-*erythro-*pentofuranosyl)iodomethane* (**23**). — Com-

pound **10** (80 mg, 0.255 mmol) was iodocyclized for 2 h to yield, after column chromatography on silica gel and elution with 99:1 benzene–ethyl acetate, **20** (52 mg) and **23** (28 mg) (72% overall yield).

Compound **20** *(higher* R_F*).* $[\alpha]_D^{20}$ +11° (*c* 1.0, chloroform); ^{1}H- (200 MHz): δ 2.06 (ddd, 1 H, $J_{2a,1}$ 4.5, $J_{2a,2b}$ 13.5, $J_{2a,3}$ 4 Hz, H-2a), 2.33 (ddd, 1 H, $J_{2b,1}$ 7, $J_{2b,3}$ 6.5 Hz, H-2b), 3.33 and 3.35 (2 H, AB part of an ABX system, $J_{1'a,1'b}$ 10, $J_{1,1'a}$ 8, $J_{1,1'b}$ 6.5 Hz, H-1'a,1'b), 3.46 and 3.49 (2 H, AB part of an ABX system, $J_{5a,5b}$ 10 Hz, $J_{5a,4}$ 5, $J_{5b,4}$ 4.5 Hz, H-5a,5b), 4.05–4.15 (m, 2 H, H-3,4), 4.33 (dddd, 1 H, H-1), 4.4–4.7 (m, 4 H, CH_2Ph), and 7.30 (s, 10 H, Ph).

Anal. Calc. for $C_{20}H_{23}IO_3$: C, 54.81; H, 5.29. Found: C, 54.54; H, 5.06.

Compound **23** *(lower* R_F*).* $[\alpha]_D^{20}$ +27° (*c* 1.1, chloroform); ^{1}H-n.m.r. (200 MHz): δ 1.76 (ddd, 1 H, $J_{2a,1}$ 9.5, $J_{2a,2b}$ 13.5, $J_{2a,3}$ 6.5 Hz, H-2a), 2.21 (ddd, 1 H, $J_{2b,1}$ 5.5, $J_{2b,3}$ 2 Hz, H-2b), 3.24 and 3.30 (2 H, AB part of an ABX system, $J_{1'a,1'b}$ 10, $J_{1,1'a}$ 6.5, $J_{1,1'b}$ 5 Hz, H-1'a,1'b), 3.46 and 3.54 (2 H, AB part of an ABX system, $J_{5a,5b}$ 10 Hz, $J_{5a,4}$ 5.5, $J_{5b,4}$ 5 Hz, H-5a,5b), 4.05–4.3 (m, 3 H, H-13,4), 4.50 and 4.55 (2s, 4 H, CH_2Ph), and 7.30 (s, 10 H, Ph).

Anal. Calc. for $C_{20}H_{23}IO_3$: C, 54.81; H, 5.29. Found: C, 54.66; H, 5.15.

*(3-O-Benzyl-2-deoxy-α-*D-erythro-*pentofuranosyl)iodomethane* **(24)** *and (3-O-Benzyl-2-deoxy-β-*D-erythro-*pentofuranosyl)iodomethane* **(21)**. — Compound **11** (130 mg, 0.414 mmol) was iodocyclized for 2 h to yield, after column chromatography, **24** (42 mg) and **21** (30 mg) (50% overall yield).

Compound **24** *(higher* R_F*).* $[\alpha]_D^{20}$ +18° (*c* 0.5, chloroform); ^{1}H-n.m.r. (200 MHz): δ 1.79 (ddd, 1 H, $J_{2a,1}$ 9.5, $J_{2a,2b}$ 13.5, and $J_{2a,3}$ 6.5 Hz, H-2a), 1.9 (m, 1 H, OH), 2.14 (ddd, 1 H, $J_{2b,1}$ 5.5, $J_{2b,3}$ 2 Hz, H-2b), 3.32 and 3.43 (2 H, AB part of an ABX system, $J_{1'a,1'b}$ 10.5, $J_{1,1'a}$ 4, $J_{1,1'b}$ 5 Hz, H-1'a,1'b), 3.58 and 3.78 (m, 2 H, after D_2O addition, the signal becomes the AB part of an ABX system, $J_{5a,5b}$ 9.5 Hz, $J_{5a,4}$ 3.5, $J_{5b,4}$ 4.5 Hz, H-5a,5b), 3.96 (dddd, 1 H, H-1), 4.05–4.2 (m, 2 H, H-3,4), 4.49 and 4.53 (2 H, ABq, *J* 11.5 Hz, CH_2Ph), and 7.32 (s, 5 H, Ph).

Anal. Calc. for $C_{13}H_{17}IO_3$: C, 44.85; H, 4.92. Found: C, 44.95; H, 4.83.

Compound **21** *(lower* R_F*).* $[\alpha]_D^{20}$ +9° (*c* 0.5, chloroform); ^{1}H-n.m.r. (200 MHz): δ 1.9 (m, 1 H, OH), 2.06 (ddd, 1 H, $J_{2a,1}$ 4.5, $J_{2a,2b}$ 13.5, $J_{2a,3}$ 4.5 Hz, H-2a), 2.32 (ddd, 1 H, $J_{2b,1}$ 6.5, $J_{2b,3}$ 6.5 Hz, H-2b), 3.3–3.8 (m, 4 H, H-1'a,1'b,5a,5b), 4.0–4.4 (m, 3 H, H-1, 3,4), 4.52 (s, 2 H, CH_2Ph), and 7.30 (s, 5 H, Ph).

Anal. Calc. for $C_{13}H_{17}IO_3$: C, 44.85; H, 4.92. Found: C, 45.28; H, 4.79.

*1,2,3-Trideoxy-6-O-triphenylmethyl-*D-erythro-*hex-1-enitol* **(12)**. — 2-Deoxy-5-*O*-triphenylmethyl-D-*erythro*-pentose (438 mg) was treated with methylenetriphenylphosphorane under the aforementioned conditions for 4 h to yield **12** (256 mg, 59%).

Anal. Calc. for $C_{25}H_{26}O_3$: C, 80.18; H, 7.00. Found: C, 79.81; H, 6.89.

*(2-Deoxy-5-O-triphenylmethyl-β-*D-erythro-*pentofuranosyl)iodomethane* **(22)** *and (2-deoxy-5-O-triphenylmethyl-α-*D-erythro-*pentofuranosyl)iodomethane* **(25)**. — Compound **12** (165 mg) was iodocyclized for 2 h to yield, after chromatography, **22** (60 mg) and **25** (62 mg) (55% overall yield).

Compound **22** *(higher* R_F*).* $[\alpha]_D^{20}$ $-3°$ (*c* 1.0, chloroform); ^{1}H-n.m.r. (200 MHz): δ 1.85 (ddd, 1 H, $J_{2a,1}$ 6, $J_{2a,2b}$ 13.5, $J_{2a,3}$ 5 Hz, H-2a), 2.34 (ddd, 1 H, $J_{2b,1}$ 6.5, $J_{2b,3}$ 7 Hz, H-2b), 2.0 (m, 1 H, OH), 3.12 and 3.25 (2 H, AB part of an ABX system, $J_{5'a,5'b}$ 10, $J_{5'a,4}$ 6, $J_{5'b,4}$ 4 Hz, H-5a,5b), 3.34 and 3.38 (2 H, AB part of an ABX system, $J_{1'a,1'b}$ 10, $J_{1,1'a}$ 6, $J_{1,1'b}$ 6.5 Hz, H-1'a,1'b), 4.09 (ddd, 1 H, $J_{3,4}$ 4 Hz, H-4), 4.26 (dddd, 1 H, H-1), 4.36 (m, 1 H, after D_2O exchange the signal becomes a ddd, H-3), and 7.2–7.5 (m, 15 H, Ph).

Anal. Calc. for $C_{25}H_{25}IO_3$: C, 60.01; H, 5.04. Found: C, 59.75; H, 4.92.

Compound **25** *(lower* R_F*).* $[\alpha]_D^{20}$ $+12°$ (*c* 1.0, chloroform); ^{1}H-n.m.r. (200 MHz): δ 1.86 (ddd, 1 H, $J_{2a,1}$ 9.5, $J_{2a,2b}$ 13.5, $J_{2a,3}$ 6.5 Hz, H-2a), 2.07 (ddd, 1 H, $J_{2b,1}$ 6.5, $J_{2b,3}$ 3 Hz, H-2b), 3.14 and 3.28 (2 H, AB part of an ABX system, $J_{1'a,1'b}$ 10, $J_{1,1'a}$ 6, $J_{1,1'b}$ 5 Hz, H-1'a,1'b), 3.23 and 3.29 (2 H, AB part of an ABX system, $J_{5a,5b}$ 10, $J_{5a,4}$ 7, $J_{5b,4}$ 5 H, H-5a,5b), 4.00 (ddd, 1 H, $J_{3,4}$ 3 Hz, H-4), 4.22 (dddd, 1 H, H-1), 4.35 (m, 1 H, after D_2O exchange the signal becomes a ddd, H-3), and 7.2–7.5 (m, 15 H, Ph).

Anal. Calc. for $C_{25}H_{25}IO_3$: C, 60.01; H, 5.04. Found: C, 59.63; H, 4.84.

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