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Towards α- or β-D-*C*-glycosyl compounds by tin-catalyzed addition of glycosyl radicals to acrylonitrile and vinylphosphonate, and flexible reduction of tetra-*O*-acetyl-α-D-glucopyranosyl bromide with cyanoborohydride☆

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Abstract

Photo-induced radical addition of acetylated α-D-glucopyranosyl bromide (**1**) to acrylonitrile or diethyl vinylphosphonate, in the presence of catalytic amounts of tri-*n*-butyltin chloride and sodium (or tetra-*n*-butylammonium) cyanoborohydride in excess, allowed efficient preparations of α-configurated nonononitrile and 2-(α-D-glucopyranosyl)-ethylphosphonate (79, 70% yields, respectively). These conditions led to 2-(α-D-manno-, and galactopyranosyl)-ethylphosphonates in 68 and 76% yields. Similarly, radical addition of acetylated 1-bromo-β-D-glucopyranosyl chloride (**2**) to acrylonitrile or diethyl vinylphosphonate afforded mainly intermediate chlorides which, upon radical reduction with excess tri-*n*-butyltin hydride, afforded the corresponding β anomers (40 and 38%, respectively) by sequential C–C and C–H bond formation. Stereocontrol relies on the α-stereoselective quenching of D-glycopyranos-1-yl radicals. We found also that UV light irradiation of **1** with excess $NaBH_3CN$ in *tert*-butanol afforded either 1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranose (65% after crystallization) or, when 10% mol thiophenol was added, 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-glucitol (79%). These are simple, tin-free, and easily controlled conditions, which compare well with known preparations of these reduced sugars.

Keywords: Glycopyranos-1-yl radicals; C-Glycosyl compounds; Acetylated sugar nitriles; Acetylated (α- and β-D-glycopyranosyl)ethylphosphonates; Acetylated 1,5-anhydro-D-glucitol; Acetylated 2-deoxy-α-D-*arabino*-hexopyranose

1. Introduction

Glycosylphosphates are essential for the bioconversions of carbohydrates, being involved in the primary metabolism, for example in glycolysis and gluconeogenesis, and in the biosynthesis of oligosaccharides, polysaccharides, and varied glycoconjugates. Among the glyco-processing enzymes mobilized by such metabolic pathways, glycosyltransferases are responsible for glycosylations. As substrates, they use either glycosyl phosphates (in non-Leloir pathways), or nucleotide diphosphate derivatives (in Leloir pathways), while dolichyl diphosphate derivatives take part in the biosynthesis of N-linked glycoproteins. Each of these glycosyl phosphates transfers a glycosyl moiety, upon cleavage of their glycosidic bond. In connection with the interest in carbohydrate mimics,[1] analogs of natural glycosyl phosphates have been investigated, and among them glycosyl phosphonates[2] which, depending on the modifications introduced, are classified as isosteric or non-isosteric to natural molecules.[2,3]

Several synthetic routes to glycosylphosphonates have been proposed. For example, access to glycosylmethylphosphonates in two steps from benzyl-protected glyconolactones, by conversion with the lithium anion of dimethyl methylphosphonate to lactol-phosphonates subsequently reduced with triethylsilane, first considered as inefficient,[2] appears now promising in the light

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of improved reduction conditions.[4] Use of aldoses in Wittig-type reactions as another approach to glycosylphosphonates showed limitations in terms of yields, and stereoselectivity.[2] Nucleophilic substitution of a glycosyl bromide with the lithium anion of dimethyl methylphosphonate was claimed to result in 1,2-elimination to afford a glycal, instead of the desired glycosylmethylphosphonate.[2] Therefore, indirect methods have been explored early,[5] based on multi-step syntheses of *C*-glycosyl compounds, either as halogenated precursors for substitution by trialkylphosphite according to the Arbuzov reaction,[2] or with an aldehyde group prone to nucleophilic attack by dialkylphosphite.[6] In the particular case of 2-glycosyl-ethylphosphonates, the base-catalyzed Michael addition of 1-deoxy-1-nitrosugars[7] or the addition of glycopyranosyl radicals[8,9] to protected vinylphosphonates are known, having a precedent with a radical-based access to nucleoside derivatives.[10] Being short routes, they appear superior to indirect approaches.[11,12] Coupling of modified glycosylphosphates and glycosylphosphonates to activated nucleotides led to stable analogs mimicking substrates of glycosyltransferases. Some were found to be good inhibitors of specific glycosyltransferases,[13,14] and their applications as regards to carbohydrate-mediated biological recognition have been discussed.[13,14]

In this context, sugar anomeric dihalides[15,16] appeared suitable precursors for preparing unknown acetylated 2-(β-D-glycopyranosyl)-ethylphosphonates by radical addition to diethyl vinylphosphonate. This idea was based on the expectation that radical addition would lead to intermediate chlorides prone to α-stereoselective radical reduction with tributyltin hydride.[17–19] Besides the β anomers expected from this approach, α anomers can be obtained in a single radical step from glycopyranosyl halides, as reported.[8,9] Each of them would be accessible precursors for preparing, upon reaction with activated nucleotides, mimics of substrates of glycosyltransferases, potentially interesting for enzymatic studies, because their opposite configurations might result in modulated bioactivities. This paper describes stereocontrolled preparations of diethyl 2-(2,3,4,6-tetra-*O*-acetyl-D-glycopyranosyl)-ethylphosphonates under radical conditions (either α, or β anomer) and preliminary observations, collected en route, concerning unprecedented photo-stimulated reductions of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide with sodium cyanoborohydride.

2. Results and discussion

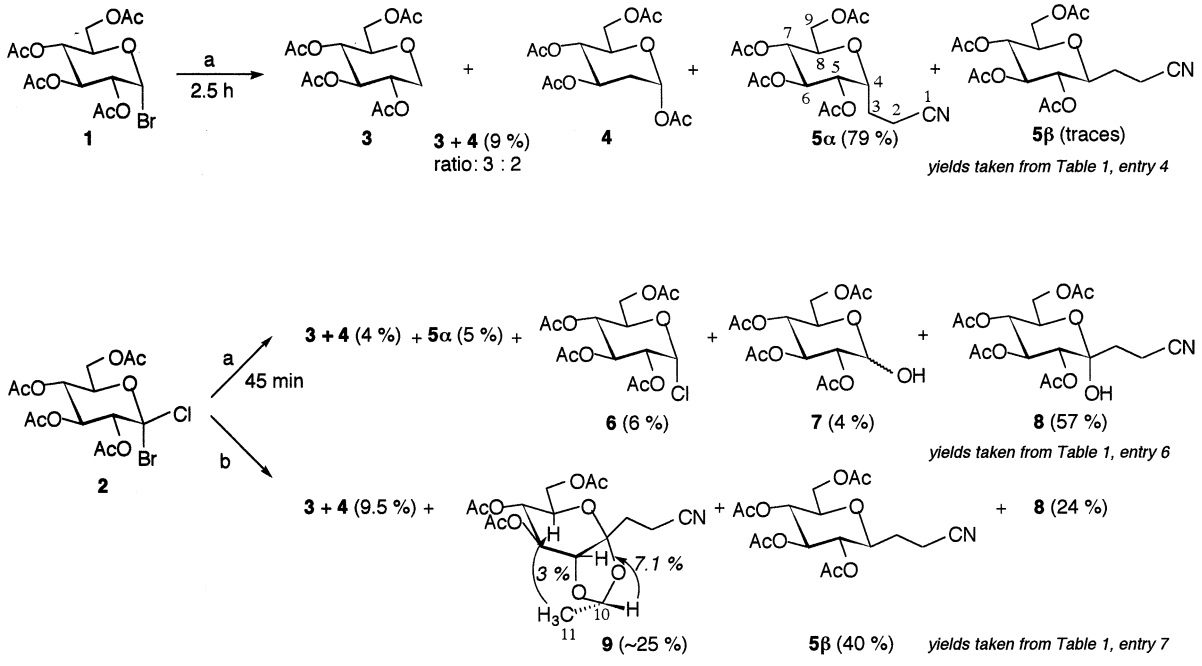
Addition of peracetylated glycopyranos-1-yl radicals to diethyl vinylphosphonate has been reported[8] to afford predominantly the corresponding α-configurated 2-glycopyranosyl-ethylphosphonates (yields in the range 17–47% from the acetobromosugars), under three related conditions (boiling Et_2O) using either tributyltin hydride (*n*-Bu_3SnH, either irradiation with halogen lamps or heating in the presence of AIBN) or tris(trimethylsilyl)silane (irradiation). Due to the stereoselective attack of glycohexopyranos-1-yl radicals,[17] the observed α/β ratio ranged from 85:15 to >98:2.[8] Optimization of this procedure in terms of yield appeared desirable, before its extension to dihalide **2**. Improvements were expected from photo-stimulated conditions due to milder reaction temperatures, and from the use of *n*-Bu_3SnH in low concentration to minimize competing hydrogen atom abstraction by glycosyl radicals, yielding reduced sugars.[17] This can be achieved easily by using *n*-Bu_3SnH (or preferably *n*-Bu_3SnCl) in catalytic amounts in the presence of such reducing agents[17] as sodium cyanoborohydride (in *tert*-butanol) or tetrabutylammonium cyanoborohydride (in benzene). In order to favor radical addition (C–C bond formation) over radical reduction (C–H bond formation), use of alkene in excess (5–12-fold excess) is also recommended.

Acrylonitrile was chosen for optimizing the radical-mediated synthesis of *C*-glycosyl compounds since the reaction products obtained from **1**[20–22] and **2**[23] are known, in part from our study of the radical addition of **2** to acrylonitrile under thermal conditions.[23] As seen from Scheme 1 and Table 1, the products obtained under UV light irradiation arose mainly from radical-mediated C–C bond formation. When *n*-Bu_3SnH was avoided, being replaced by *n*-Bu_3SnCl (entry 4), the yield of **5α** reached 79%, a value found higher than those published, [21,22] while the reduced sugars were isolated in a ~10% yield only. Therefore, a molar ratio sugar–*n*-Bu_3SnCl–reducing agent–alkene equal to 1:0.3:~2:5 (see Tables 1 and 2) was fixed as a good compromise throughout this work. 2,3,4,6-Tetra-*O*-acetyl-1,5-anhydro-D-glucitol (**3**)[24,25] and 1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranose (**4**),[26–28] having similar TLC mobilities, were distinguished by ^1H NMR. In the absence of *n*-Bu_3SnH, the rearranged 2-deoxy sugar **4** was clearly observed (entry 5).

Treatment of dihalide **2** under the same conditions (entry 6) afforded compound **8** in 57% isolated yield. The product distribution showed that radical addition to acrylonitrile (**5α**: 5%; **8**: 57%) predominated over mono-reduction (**6**: 6%; **7**: 4%) and double-reduction (**3**/**4**: 4%). One simple explanation to the formation of **8** involves hydrolysis of a labile halogenated precursor.[19,23] So, in further experiments (entries 7–11) the reaction mixture was reacted with excess *n*-Bu_3SnH, added either directly to the reaction medium (entry 11), or after concentration under reduced pressure and addition of benzene as solvent (entries 7–10). These experiments led to **5β** in varying yields (up to 40%), with no detectable trace (NMR) of the α anomer in accordance

with the high α-stereoselectivity of hydrogen atom abstraction by C-1-substituted hexopyranosyl radicals.[17,18] The intermediate chloride underwent other competing reactions to afford **8** and **9** whose structure was established by NMR (nOe enhancements pointed to the endo orientation of the H_3C-11 group and vicinal couplings $J_{5,6}$ 2.6, $J_{6,7}$ 1.7 Hz indicated a distorted D-glucopyranosyl ring, as showed in Scheme 1).[29,30] Use of $NaBH_3CN$ from a recently purchased batch favored formation of **9**, and did not prevent that of the product **8** (entries 10, 11), which might arise also from radical quenching with molecular oxygen.[31] Formation of **9** via radical intermediates seems improbable, because of the absence of any synthetic precedent based on radical approaches.[18,27,28,32] The conversion of 1,2-*trans* acylglycosyl halides into 1,2-*O*-alkylidene[33–35] by $NaBH_4$-mediated reductive attack of 1,3-dioxolenium ions is well known. Due to the α-stereoselective quenching of D-glucopyranos-1-yl radicals, the chloride initially formed in the radical addition is expected to have a β-oriented chlorine atom. Hence, chloride displacement by the vicinal acetoxy group could afford a 1,3-dioxolenium ion easily. Its reduction to **9** should involve $NaBH_3CN$ rather than *n*-Bu_3SnH, being present in low concentration.

Photo-initiated addition of radicals derived from halides **1** and **2** to diethyl vinylphosphonate was investigated next (Scheme 2, Table 2). Use of *n*-Bu_3SnCl with varying amounts of $NaBH_3CN$ in *tert*-butanol (entries 1–3) showed that, with 1.5 equiv of the reducing agent, radical addition to diethyl vinylphosphonate predominated, **12α** being isolated in 70% yield (entry 3). With other acetylated α-D-hexopyranosyl bromides (**10**: D-manno, **11**: D-galacto), the corresponding 2-(α-D-glycopyranosyl)-ethylphosphonates **13** and **14** were obtained in 68 and 76% yield, respectively, significantly higher than those reported.[8] Isolation of a 1,2-*O*-ethylidene derivative was achieved in the D-*manno* series only, (*R*/*S*)-3,4,6-tri-*O*-acetyl-1,2-*O*-ethylidene-β-D-mannopyranose[34] being obtained in 12% yield, from the 1,2-*trans* related 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide (**10**). This data is in keeping with the proposed reaction path to **9**. When dihalide **2** was reacted with diethyl vinylphosphonate in the presence of *n*-Bu_3SnCl and either $NaBH_3CN$ or *n*-Bu_4N BH_3CN, radical addition led to **15** and **16** in 28–36% total yield (entries 5, 6). The β anomer **12β** could be obtained from **2** by a sequential one-pot procedure (entries 7–9) in up to 38% yield (entry 8). All these results showed that addition of hexopyranos-1-yl radicals to such electron-poor alkenes as acrylonitrile or diethyl vinylphosphonate can be controlled to afford in uniform yields either α-configurated *C*-glycosyl derivatives[17] (**5α**: 79%, **12α**: 70%, **13**: 68%, **14**: 76% from acetobromosugars) or the β anomers[18,19] in two steps from the anomeric dihalide **2** (**5β**: 40%, **12β**: 38%). Syntheses of stable substrate analogs of glycosyltransferases from the glycosylphosphonates described herein are underway and will be reported in due course.



Scheme 1. (a) Acrylonitrile, 5 equiv; *n*-Bu_3SnCl, 0.3 equiv; $NaBH_3CN$, 2 equiv; *tert*-butanol; AIBN; UV light irradiation (Vycor filter); reaction temperature, ~30–35 °C. (b) (1) Acrylonitrile, 5 equiv; *n*-Bu_3SnCl, 0.3 equiv; $NaBH_3CN$, 2 equiv; *tert*-butanol; AIBN; UV light irradiation (Vycor filter); 30 min; (2) *tert*-butanol replaced by benzene; *n*-Bu_3SnH, 4 equiv; AIBN; UV light irradiation (Vycor filter); 15 min.

Table 1
Addition of radicals derived from **1** and **2** to acrylonitrile [a] with either *n*-Bu_3SnH (A) or catalytic *n*-Bu_3SnCl (B) and $NaBH_3CN$ (C) [b]

Entry	Halide (mmol)	Reductant (equiv)	Solvent (mL)	Time (h)	Products (%) [c]						
					3–4 [d]	**5α**	**5β**	**6**	**7**	**8**	**9**
1	**1**, 10	A: 1+0.4	Et_2O, 20 [e]	4+39	19 (>95/5)	37	3				
2	**1**, 5	A: 1.1+0.4	Et_2O, 10 [f]	4+6	15 (>95/5)	49	2				
3	**1**, 0.5	A+C 0.3+2	*t*-BuOH, 12 [g]	2	12	56	1.5				
4	**1**, 0.5	B+C 0.3+2	*t*-BuOH, 12 [g]	2.5	9 (3/2)	79					
5	**1**, 0.12	B+C 0.3+2	*t*-BuOH, 3 [g]	2.5	13 (~3/2)	60					
6	**2**, 0.5	B+C 0.3+2	*t*-BuOH, 12 [h]	0.75	4	5		6	4	57	
7	**2**, 0.5	B+C 0.3+2	*t*-BuOH, 11.5 [g] benzene, 7	0.5 [i] 0.35 [j]	9.5		40			24	
8	**2**, 0.5[k]	B+C 0.3+2	*t*-BuOH, 11.5 [g] benzene, 12	0.5 [i] 0.25 [j]	11		24			30	
9	**2**, 0.5 [k]	B+C 0.3+2	*t*-BuOH, 11.5 [g] benzene, 12	0.5 [i] 0.25 [j]						40	24
10	**2**, 0.25	B+C [l] 0.3+2	*t*-BuOH, 5 [g] benzene, 8	0.75 [i] 0.5 [j]	12					28	27
11	**2**, 0.5 [k]	B+C [l] 0.3+1.5	*t*-BuOH, 8	0.5 [i] 0.5 [j]	6		10 [m]			21	32 [m]

[a] Unless indicated otherwise, all reactions were carried out at ~35 °C under argon, using a medium pressure mercury lamp (Hanovia, 450 W), equipped with a Vycor filter ($\lambda > 254$ nm) and inserted in a two-wall jacket made of quartz with a tap water flow for cooling. The reaction mixture was introduced into a quartz tube (~13 mL volume, 13 mm external diameter) equipped with a stirring bar. Acrylonitrile was used in excess (5 equiv, unless otherwise noted) while AIBN was used in catalytic amounts, as indicated. Except for run 6, the transformation of **2** involved two steps: first, radical addition to acrylonitrile in *t*-BuOH and then radical reduction of an intermediate chloride with *n*-Bu_3SnH (4 equiv) plus AIBN (0.6 equiv) in benzene. Therefore, unless otherwise stated, after conversion of **2**, *t*-BuOH was evaporated under reduced pressure and replaced with benzene.

[b] First, $NaBH_3CN$ taken from a batch kept for an undetermined period in an excicator was used, but control experiments were carried out with $NaBH_3CN$ from a recently purchased batch, as indicated.

[c] Isolated yields.

[d] The **3**:**4** ratio, when estimated by ^1H NMR, is given in parenthesis.

[e] The reaction medium was introduced in a round-bottomed pyrex flask and refluxed with a 250 W sun lamp placed below the flask. After boiling the ethereal solution for 4 h, the solids were filtered off. More acrylonitrile (2.4 equiv), *n*-Bu_3SnH (0.4 equiv), and AIBN (0.03 equiv) were added to the mixture before heating for 39 h.

[f] After irradiation with filtered UV light for 4 h, the solids formed were filtered off. More acrylonitrile (2.4 equiv), *n*-Bu_3SnH (0.4 equiv), and AIBN (0.03 equiv) were added to the mixture before exposure to UV light for 6 h.

[g] With 0.6 equiv AIBN.

[h] With 0.3 equiv AIBN.

[i] One-pot reaction: irradiation time for the addition step.

[j] One-pot reaction: irradiation time for the reduction step.

[k] A larger quartz tube was used (~94 mL volume; 27 mm external diameter) for exposure to unfiltered UV light.

[l] $NaBH_3CN$ from a recently purchased batch.

[m] Estimated yields based on the ^1H NMR analysis of a mixture (81 mg, **5β**–**9** in 3:1 ratio) collected after column chromatography.

The aforementioned addition reactions were believed to be mediated mainly by tin radicals, and that view was confirmed by a blank experiment. When the addition of **1** to acrylonitrile was attempted under irradiation (4 h) with $NaBH_3CN$ and AIBN, but without any *n*-Bu_3SnH–*n*-Bu_3SnCl added, compound **5α** was isolated in low yield (9%). Interestingly, **1** was converted mainly into **3**–**4** (53% yield), with the rearranged product **4** being predominant (**3**–**4** ratio: 17:83). Therefore, under such tin-free conditions, formation of **4** and

5α occurred, suggesting the operation of competing radical processes, not based on tin. Without acrylonitrile, enhanced yield of **3**–**4** was expected. Indeed, exposure of a mixture of **1** and $NaBH_3CN$ in *tert*-butanol to filtered UV light for ~0.5 h resulted in a clean reaction, visualized by a new single spot on TLC plates. Simple workup led to crude products, shown by ^1H NMR spectroscopy to contain essentially **4**, in admixture with **3** (**4**–**3** ratio: ~95:5). These experiments led reproducibly to pure **4** as nice colorless prisms in 60–65% yield (Scheme 3), under simple and inexpensive conditions. In spite of somewhat lower yields, the proposed method is advantageous, as compared to radical methods using either tin hydride (slow hydride addition required,[27,28] difficulties due to toxicity, and elimination of organotin compounds[18]) or costly tris(trimethylsilyl)silane,[36] and compared also with the conversion of **1** into 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol (triacetyl-D-glucal), followed by addition of either acetic acid (crude **4**, 98.4%, α/β ratio: 71:29)[37] or water, to give 3,4,6-tri-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranose (67% yield, α/β mixture).[38]

The suspicion that conversion of **1** into **4** proceeded via radical intermediates[27,28] was reinforced by a further experiment based on the concept of polarity reversal catalysis.[39] While the electrophilic character of D-glycopyranos-2-yl radicals makes them prone to hydrogen atom abstraction from cyanoborohydride anion or

Table 2
Addition of radicals derived from **1** and **2** to diethyl vinylphosphonate [a] with catalytic *n*-Bu_3SnCl (B) and either $NaBH_3CN$ [b] (C) or *n*-Bu_4NBH_3CN (D)

Entry	Halide (mmol)	Reductant (equiv)	Solvent (mL)	Time (h)	Products (%) [c]					
					3–**4** [d]	**7**	**12α**	**12β**	**15**	**16**
1	**1**, 0.49	B+C 0.3+2	*t*-BuOH, 8	0.6	26 (47/53)	3	55			
2	**1**, 0.49	B+C 0.3+1.5	*t*-BuOH, 8	0.8	13 (47/53)	3	63			
3	**1**, 1.5	B+C [e] 0.3+1.5	*t*-BuOH, 24	1	8 (39/61)	3	70			
4	**1**, 0.49	B+D 0.3+1.5	benzene, 8	9	8	25	38			
5	**2**, 0.45	B+C 0.3+1.5	*t*-BuOH, 8	0.6					10	18
6	**2**, 0.45	B+D 0.3+2	benzene, 6	1					18	18
7	**2**, 0.68 [f]	B+D 0.3+2	benzene, 9	1 [g] 0.25 [h]	21 (>95/5)	34		27		8
8	**2**, 0.68 [f]	B+D 0.3+2	benzene, 8 [i]	1.5 [g] 0.5 [j]	29 (>95/5)	9		38		7
9	**2**, 0.68 [f]	B+D 0.3+1.5	benzene, 8 [i]	2.5 [g] 0.35 [j]	24 (>95/5)	5		20		2

[a] The reaction mixture, containing diethyl vinylphosphonate (5 equiv), *n*-Bu_3SnCl (0.3 equiv), AIBN (0.6 equiv), sodium or tetra-*n*-butyl ammonium cyanoborohydride in the selected solvent, as indicated, was introduced into a quartz tube (~94 mL volume, 27 mm external diameter) equipped with a stirring bar. Argon was bubbled into the liquid until the sugar halide get dissolved (~0.5/1.5 h). All reactions were carried out at ~35 °C under argon, using a medium pressure mercury lamp (Hanovia, 450 W), equipped with a Vycor filter ($\lambda > 254$ nm) and inserted into a two-wall jacket made of quartz and cooled with a tap water flow. Some one-pot type experiments carried out with **2** involved first a radical addition to diethyl vinylphosphonate, then radical reduction of the intermediate chloride **15** in benzene with excess *n*-Bu_3SnH (3 equiv, or more), as indicated.

[b] As indicated, $NaBH_3CN$ was taken either from a recently purchased batch or from a batch kept for an undetermined period in an excicator.

[c] Isolated yields.

[d] The **3**:**4** ratio, given in parenthesis, was estimated by ^1H NMR.

[e] $NaBH_3CN$ was taken from a recently purchased batch.

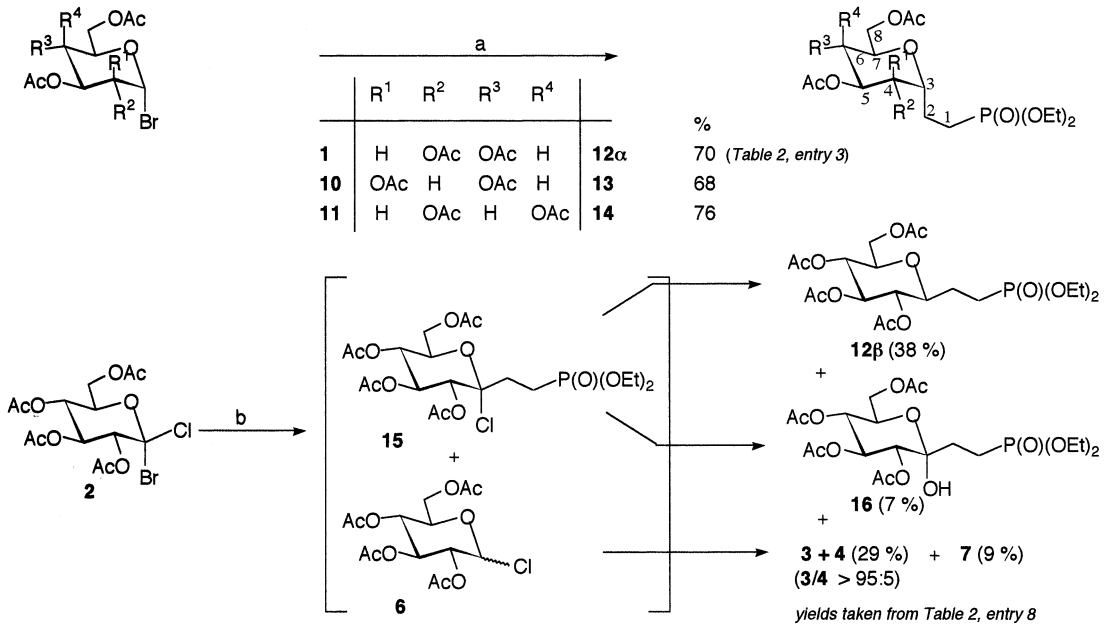
[f] Radical-based addition and reduction carried out in one pot.

[g] Irradiation time for the addition step.

[h] Irradiation time for the reduction step with 10 equiv *n*-Bu_3SnH.

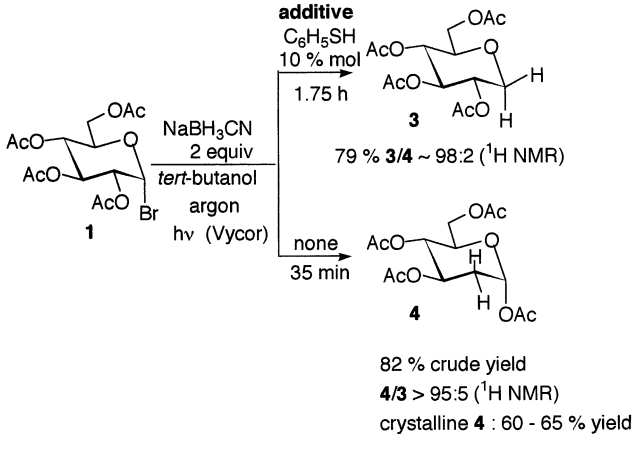
[i] Argon was bubbled through the liquid for ~2 h.

[j] Irradiation time for the reduction step with 3 equiv *n*-Bu_3SnH.



Scheme 2. (a) Diethyl vinylphosphonate, 5 equiv; n-Bu_3SnCl, 0.3 equiv; $NaBH_3CN$, 1.5 equiv; *tert*-butanol; AIBN; UV light irradiation (Vycor filter); temperature, ~30–35 °C. (b) (1) Diethyl vinylphosphonate, 5 equiv; n-Bu_3SnCl, 0.3 equiv; n-Bu_4NBH_3CN, 2 equiv; benzene; AIBN; UV light irradiation (Vycor filter); (2) n-Bu_3SnH, 3 equiv; AIBN; UV light irradiation (Vycor filter).

related species, anomeric radicals are nucleophilic and abstract hydrogen atom from thiols and selenols readily.[18] This accounts to the fact that the presence of catalytic amounts of thiols/selenols prevents formation of 2-deoxy sugars by radical rearrangement under poorly hydrogen-donating conditions, thus favoring formation of anhydro-itols.[40] This expectation was founded, since under the aforementioned conditions, but with 10 mol% thiophenol added, almost pure 1,5-anhydro-D-glucitol was isolated by chromatography in 79% yield (**3**–**4** ratio: ~98:2), a result which compares well with other routes to **3**.[18,22] Hence, adding 10 mol% thiophenol modified dramatically the reduction issue, resulting in a simple and efficient synthesis of acetylated 1,5-anhydro-D-glucitol from tetra-*O*-acetyl-α-D-glucopyranosyl bromide, whereas the rearranged 1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranose was formed with $NaBH_3CN$ alone (Scheme 3). Worth of note are the high flexibility of these reductions, and the unprecedented use of $NaBH_3CN$. Its photo-reactivity appears to be poorly developed.[41] Therefore, ongoing investigations to establish the scope, limitations, and mechanisms of such reductions are in progress and will be reported soon.



Scheme 3.

3. Experimental

General methods.—Benzene and *tert*-butanol were distilled over CaH_2 and under argon atmosphere. Diethyl vinylphosphonate (97% grade), $NaBH_3CN$ (95% grade) and Bu_4NBH_3CN were purchased from Aldrich, and used as received. Air was removed from the reaction media by bubbling argon into organic solutions for 0.5–1.5 h. For photo-induced transformations, except that mentioned in Table 1, entry 1, deoxygenated solutions introduced into a quartz tube (small one: ~13 mL volume, 13 mm external diameter or large one: ~94 mL volume, 27 mm external diameter) placed near (~1 cm) a medium pressure mercury lamp (Hanovia, 450 W) equipped with a Vycor filter ($\lambda > 254$ nm) were irradiated under an argon atmosphere and

magnetic stirring (the lamp was inserted into a two-wall device made of quartz and allowing circulation of tap water for cooling purpose). NMR spectra were recorded with Bruker spectrometers AC 200, DRX 300, and DRX 500 for solutions in $CDCl_3$. Chemical shifts (δ) are in ppm (reference: Me_4Si); coupling constants (Hz) other than ^3J are specified with the appropriate superscript. ^{31}P NMR spectra were recorded with Bruker spectrometers at 81 MHz (AC 200) or 121.5 MHz (DRX 300) from $CDCl_3$ solutions with H_3PO_4 as the external reference. Mass spectra were measured with a Finnigan Mat 95 XL spectrometer. Other details have been published recently.[19,31]

5,6,7,9-Tetra-O-*acetyl-2,3-dideoxy*-α-D-gluco-*4-nonulopyranononitrile* (**8**).—A solution containing 2,3,4,6-tetra-*O*-acetyl-1-bromo-β-D-glucopyranosyl chloride (**2**)[15] (222 mg, 0.5 mmol), acrylonitrile (132.5 mg, 2.5 mmol), *n*-Bu_3SnCl (48.8 mg, 0.15 mmol), $NaBH_3CN$ (62.8 mg, 1 mmol), and AIBN (25 mg, 0.15 mmol) in *tert*-butanol (12 mL) was introduced into a quartz tube (13 mm external diameter). While stirring the solution under an argon atmosphere, irradiation with filtered UV light was applied for 45 min, whereupon TLC monitoring showed the transformation of the starting material into five products. After concentration under reduced pressure, the residue was taken up in CH_2Cl_2. The organic phase was washed with water, then dried (Na_2SO_4), and concentrated to a residue which was dissolved in MeCN. Organotin compounds were removed by washing the MeCN phase with pentane (3 × 15 mL). Upon concentration and chromatography of the mixture on a column of silica gel eluted with 2:3 EtOAc–petroleum ether, concentration of homogeneous fractions led to the following products: **6** (R_f 0.65, 11 mg, 0.03 mmol, 6% yield), **3**–**4** (R_f 0.3, 6.2 mg, 0.02 mmol, 4% yield), **5α** (R_f 0.18, 10.1 mg, 0.026 mmol, 5% yield), **7** (R_f 0.14, 7 mg, 0.02 mmol, 4% yield), and **8** (R_f 0.1, 115.2 mg, 0.28 mmol, 57.4% yield).

8: colorless crystals, mp 102–105 °C (Et_2O–petroleum ether); R_f 0.1 in 2:3 EtOAc–petroleum ether; $[\alpha]_D^{20}$ +33° (*c* 0.6, CH_2Cl_2); IR (KBr) *v* 3400 (OH), *v* 2240 (CN), and *v* 1750 cm^{-1} (CO); ^1H NMR (200.13 MHz, $CDCl_3$): δ 5.45 (t, 1 H, $J_{6,7}$ 9.6 Hz, H-6), 5.09 (t, 1 H, $J_{7,8}$ 9.7 Hz, H-7), 4.96 (d, 1 H, $J_{5,6}$ 9.7 Hz, H-5), 4.25 (dd, 1 H, $J_{9a,9b}$ 11.6, $J_{8,9a}$ 5.8 Hz, H-9a), 4.12 (dd, 1 H, H-9b), ~4.2 (m, 1 H, H-8), ~3.5 (br s, 1 H, OH), 2.56 (m, 2 H, H-2a, H-2b), 2.11, 2.09, 2.03, 2.00 (4s, 12 H, acetyl), ~2.0 (m, 2 H, H-3a, H-3b); nOe difference spectra recorded for a $CDCl_3$ solution of **8** showed, on selective saturation at 2.5 ppm (H_2C-2), enhancements (ppm, %) of the following resonances: H_2C-3 (~2.0, 6%) and H-5 (4.96, 4%). Selective saturation at ~2.0 (H_2C-3) resulted in enhancements (ppm, %) of the H_2C-2 (2.56, 16%) and H-5 (4.96, 9%) resonances, in support of the methylene carbons attribution; ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 171.2, 170.6, 170.0, 169.9 (C=O), 119.8 (C-1), 96.5 (C-4), 72.5 (C-5), 71.5 (C-6), 69.1 (C-8), 68.5 (C-7), 62.1 (C-9), 34.2 (C-3), 21.15, 21.03, 21.02, 21.00 (acetyl), 11.2 (C-2). Anal. Calcd for $C_{17}H_{23}NO_{10}$ (387): C, 50.87; H, 5.78; N, 3.49; O, 39.86. Found: C, 50.95; H, 5.71; N, 3.49; O, 39.59.

*(10*R*)-6,7,9-Tri*-O-*acetyl-2,3-dideoxy-4,5-ethylidene*-α-D-gluco-*4-nonulopyranononitrile* (**9**).—A solution prepared as before for the radical addition of **2** (0.5 mmol) to acrylonitrile was irradiated for 30 min, whereupon the solvent was evaporated under reduced pressure. The residue was dissolved in benzene (12 mL), and after adding *n*-Bu_3SnH (580 mg, 2 mmol) and AIBN (25 mg, 0.15 mmol) to the solution introduced into a quartz tube, irradiation was applied for 15 min. Benzene was evaporated under diminished pressure and the residue was diluted in CH_2Cl_2, washed with water and dried ($MgSO_4$). After filtration and concentration, the product mixture was freed from organotin compounds by washing an MeCN solution with pentane (3 × 15 mL). Chromatography on silica gel with 2:3 EtOAc–petroleum ether as the mobile phase afforded **3**–**4**, **5β**, **8**, and **9** (see Table 1). Compound **9** being only slightly more mobile than **5β** could be obtained in pure state after repeated chromatography.

9: Colorless oil; $[\alpha]_D^{22}$ +31.6° (*c* 1.2, CH_2Cl_2); ^1H NMR (200.13 MHz, $CDCl_3$): δ 5.17 (dd, 1 H, $J_{5,6}$ 2.6, $J_{6,7}$ 1.7 Hz, H-6), 5.03 (q, 1 H, $J_{10,11}$ 4.9 Hz, H-10), 4.83 (dt, 1 H, $J_{7,8}$ 9.5 Hz, H-7), 4.17 (d, 2 H, *J* 4 Hz, H-9a, H-9b), 4.07 (dt, 1 H, $J_{8,9a} = J_{8,9b}$ 4.1 Hz, H-8), 3.79 (dd, 1 H, $^4J_{5,7}$ 0.9 Hz, H-5), 2.61 (dd, 2 H, *J* 6.9, *J* 8.8 Hz, H-2a, H-2b), ~2.10 (m, 2 H, H-3a, H-3b), 2.13, 2.10, 2.09 (acetyl), 1.49 (d, 3 H, endo-H_3C-11); nOe difference spectra recorded for a $CDCl_3$ solution of **9** showed, on selective saturation at 1.5 ppm (H_3C-11), enhancements (ppm, %) of the following resonances: HC-10 (5.03, 5.7%) and H-8 (4.07, 3%). Selective saturation at 5.03 ppm (HC-10) resulted in enhancements (ppm, %) of the H-5 (3.79, 7.1%) and H_3C-11 (1.5, 7.3%) resonances, in support of the endo and exo orientations of, respectively, the H_3C-11 group and the HC-10 hydrogen atom; ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 170.7, 169.8, 169.0 (C=O), 119.6 (CN), 102.7 (C-4), 100.9 (C-10), 77.5 (C-5), 70.3 (C-6), 68.4 (C-7), 67.0 (C-8), 63.1 (C-9), 33.9 (C-3), 20.9, 20.8, 20.8 (acetyl), 19.2 (C-11), 11.4 (C-2). MS (CI, isobutane): *m*/*z* 386 (17) $[M+H]^+$, 342 (53) $[M+H-CH_3CHO]^+$, 282 (6.5) $[M+H-CH_3CHO-CH_3COOH]^+$, 222 (100) $[M+H-CH_3CHO-2CH_3COOH]^+$, 162 (34.6) $[M+H-CH_3CHO-3CH_3COOH]^+$. HRMS Calcd for $C_{17}H_{24}NO_9$ [M + H] 386.145106. Found: 386.14503.

Diethyl 2-(2,3,4,6-tetra-O-*acetyl*-α-D-*glucopyranosyl)-ethylphosphonate* (**12α**).—A solution of **1** (604.1 mg, 1.47 mmol), *n*-Bu_3SnCl (125 μL, 0.44 mmol, 0.3 equiv), $NaBH_3CN$ (95% grade, 148.5 mg, 2.21 mmol, 1.5 equiv), diethyl vinylphosphonate (1.17 mL, 7.35 mmol, 5 equiv), and AIBN (146.9 mg, 0.88 mmol, 0.6

equiv) in freshly distilled *tert*-butanol (24 mL) was introduced in a quartz tube (~94 mL volume, 27 mm external diameter) equipped with a magnetic bar. While stirring under an argon atmosphere, the reaction mixture was irradiated with filtered UV light for 50 min, whereupon TLC monitoring (1:1 EtOAc–petroleum ether) showed complete transformation of **1** (R_f 0.70) into reduced products **3**–**4** (R_f 0.65), 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (**7**) (R_f 0.48), and diethyl 2-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-ethylphosphonate (R_f 0.03). After concentration under diminished pressure, the oily residue was dissolved in CH_2Cl_2 (~30 mL), and after washing the organic phase with water (3 × 30 mL), it was dried ($MgSO_4$), filtered, and concentrated under diminished pressure. The residue was taken up in CH_3CN (~30 mL), and the organotin compounds were removed by washing with hexane (3 × 30 mL). Concentration and chromatography on a column of silica gel eluted with 1:1.5 EtOAc–petroleum ether afforded **3**–**4** (40.8 mg, 0.123 mmol, 8% yield, **3**–**4** ratio: 39:61). Further elution with 20:1 EtOAc–ethanol as the mobile phase gave **7** (17 mg, 0.05 mmol, 3%), and **12α** (510.0 mg, 1.03 mmol, 70%) as an oil. **12α**: R_f 0.36 in 20:1 EtOAc–ethanol; $[\alpha]_D^{25}$ +47° (*c* 1, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$):[8] δ 5.31 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-5), 5.10 (dd, 1 H, $J_{3,4}$ 5.7 Hz, H-4), 4.98 (t, 1 H, $J_{6,5}$ 9.5 Hz, H-6), 4.24 (dd, 1 H, $J_{7,8a}$ 5.5, $J_{8a,8b}$ 11.9 Hz, H-8a), 4.16–4.05 (m, 6 H, H-3, H-8b, 2 OCH_2CH$_3$), 3.81 (m, 1 H, H-7), 2.09, 2.08, 2.06, 2.03 (4s, 12 H, acetyl), 1.92–1.60 (m, 4 H, H-1a, H-1b, H-2a, H-2b), 1.34 (dt, 6 H, *J* 7, $^4J_{H,P}$ 1.3 Hz, 2 OCH$_2$CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.4, 169.9, 169.5, 169.4 (4s, C=O), 72.4 (d, $J_{C\text{-}3,P}$ 16.8 Hz, C-3), 70.1 (C-5), 70.0 (C-4), 68.7 (C-7), 68.6 (C-6), 62.2 (C-8), 61.6 (d, 2 C, $^2J_{C,P}$ 6.5 Hz, OCH$_2$CH$_3$), 21.1 (d, $^1J_{C\text{-}1,P}$ 144.3 Hz, C-1), 20.6, 20.6, 20.5, 20.5 (acetyl), 18.9 (d, $^2J_{C\text{-}2,P}$ 3.9 Hz, C-2), 16.4 (d, 2C, $J_{CH\text{-}3,P}$ 5.9 Hz, OCH$_2$CH_3); ^{31}P NMR (81 MHz, $CDCl_3$): δ 31.54; MS (FAB$^+$, glycerol + LiCl): *m*/*z* 503.2 [M + Li]$^+$; Anal. Calcd for $C_{20}H_{33}O_{12}P$ (496.44): C, 48.39; H, 6.70; P, 6.24. Found: C, 48.43; H, 6.72; P, 6.31.

Diethyl 2-(2,3,4,6-tetra-O-*acetyl-α*-D-*mannopyranosyl)-ethylphosphonate* (**13**).—As described for **12α**, this product was prepared from 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide (**10**) (550.8 mg, 1.34 mmol, reaction time: 55 min) in 68% yield. The following products were recovered successively from the column (with 2:3 EtOAc–petroleum ether as the mobile phase): 3,4,6-tri-*O*-acetyl-1,2-*O*-ethylidene-β-D-mannopyranose[34] as a ~9:1 *R*/*S* mixture (R_f 0.39, 49.5 mg, 0.15 mmol, 12%), 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-mannitol[42,43] (R_f 0.33, 50.0 mg, 0.151 mmol, 12%), 2,3,4,6-tetra-*O*-acetyl-D-mannopyranose (R_f 0.20, 29 mg, 0.083 mmol, 6%), and upon elution with 20:1 EtOAc–ethanol, **13** (R_f 0.57, 454 mg, 0.915 mmol, 68%).

13: syrup; $[\alpha]_D^{25}$ +8° (*c* 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.24 (dd, 1 H, $J_{4,5}$ 3.3, $J_{5,6}$ 8.3 Hz, H-5), 5.17 (t, 1 H, $J_{6,7}$ 8.3 Hz, H-6), 5.15 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-4), 4.39 (dd, 1 H, $J_{7,8a}$ 6.6, $J_{8a,8b}$ 12.3 Hz, H-8a), 4.19–4.05 (m, 4 H, 2 OCH_2CH$_3$), 4.10 (dd, 1 H, $J_{7,8b}$ 2.5 Hz, H-8b), 3.95 (dt, 1 H, $J_{2,3}$ 10.9 Hz, H-3), 3.87 (ddd, 1 H, H-7), 2.12, 2.10, 2.08, 2.05 (4s, 12 H, acetyl), 2.10–1.60 (m, 4 H, H-1a, H-1b, H-2a, H-2b), 1.34 (dt, 6 H, $^4J_{H,P}$ 2.3, $J_{H,H}$ 7.1 Hz, 2 OCH$_2$CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 170.4, 170.0, 169.6, 169.5 (4s, C=O), 73.5 (d, $J_{C\text{-}3,P}$ 16.8 Hz, C-3), 70.7 (C-7), 69.9 (C-4), 68.4 (C-5), 66.9 (C-6), 62.0 (C-8), 61.6 (d, 2 C, $^2J_{C,P}$ 6.2 Hz, OCH_2CH$_3$), 22.1 (d, $^2J_{C,P}$ 4.3 Hz, C-2), 21.3 (d, $^1J_{C\text{-}1,P}$ 143.6 Hz, C-1), 20.7, 20.6, 20.6, 20.5 (acetyl), 16.3 (d, 2 C, $J_{CH\text{-}3,P}$ 5.6 Hz, OCH$_2$CH_3); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 32.05; Anal. Calcd for $C_{20}H_{33}O_{12}P$ (496.44): C, 48.39; H, 6.70; P, 6.24. Found: C, 47.05; H, 6.83; P, 6.14.

Diethyl 2-(2,3,4,6-tetra-O-*acetyl-α*-D-*galactopyranosyl)-ethylphosphonate* (**14**).—As indicated for **12α**, this product was prepared from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**11**) (579.3 mg, 1.41 mmol, reaction time: 40 min) in 76% yield. A ~7:3 inseparable mixture of 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-galactitol[25] and 1,3,4,6-tetra-*O*-acetyl-α-D-*lyxo*-hexopyranose[28] (R_f 0.78 in 1:1 EtOAc–petroleum ether, 59 mg, 0.18 mmol, 13%) was recovered first from the column. **14**: syrup; R_f 0.48 in 20:1 EtOAc–ethanol; $[\alpha]_D^{25}$ +61° (*c* 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.41 (dd, 1 H, $J_{5,6}$ 3.3, $J_{6,7}$ 2.5 Hz, H-6), 5.29 (dd, 1 H, $J_{3,4}$ 5.2, $J_{4,5}$ 9.2 Hz, H-4), 5.19 (dd, 1 H, H-5), 4.23 (dd, 1 H, $J_{7,8a}$ 7.7, $J_{8a,8b}$ 11.4 Hz, H-8a), 4.23–4.14 (m, 6 H, H-3, H-8b, 2 OCH_2CH$_3$), 4.00 (ddd, 1 H, $J_{7,8b}$ 4,8 Hz, H-7), 2.13, 2.09, 2.06, 2.03 (4s, acetyl), 1.34 (dt, 6 H, $^4J_{H,P}$ 1.8, $J_{CH\text{-}2,CH\text{-}3}$ 7.0 Hz, 2 OCH$_2$CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 170.1, 169.8, 169.7 (4 C=O), 71.7 (d, $J_{C,P}$ 16.5 Hz, C-3), 68.0 (C-7), 67.9 (C-4), 67.6 (C-5), 67.3 (C-6), 61.6 (d, $^2J_{C,P}$ 6.5 Hz, OCH_2CH$_3$), 61.6 (d, $^2J_{C,P}$ 6.6 Hz, OCH_2CH$_3$), 61.3 (C-8), 21.2 (d, $^1J_{C,P}$ 143.9 Hz, C-1), 20.6, 20.5 (2 C), 20.45 (acetyl), 19.6 (d, $^2J_{C,P}$ 3.5 Hz, C-2), 16.3 (d, 2 C, $J_{C,P}$ 6.0 Hz, OCH$_2$CH_3); ^{31}P NMR (81 MHz, $CDCl_3$): δ 31.7; Anal. Calcd for $C_{20}H_{33}O_{12}P$ (496.44): C, 48.39; H, 6.70; P, 6.24. Found: C, 48.48; H, 7.54; P, 6.28.

Diethyl 2-(2,3,4,6-tetra-O-*acetyl-β*-D-*glucopyranosyl)-ethylphosphonate* (**12β**).—A solution of **2**[15] (300 mg, 0.676 mmol), *n*-Bu_3SnCl (60 μL, 0.2 mmol, 0.3 equiv), Bu_4NBH_3CN (382 mg, 1.15 mmol, 2 equiv), diethyl vinylphosphonate (540 μL, 3.38 mmol, 5 equiv), and AIBN (67 mg, 0.41 mmol, 0.6 equiv) in dry oxygen-free benzene (8 mL) was introduced in a quartz tube (~94 mL volume; 27 mm external diameter) equipped with a magnetic bar. While stirring under an argon atmosphere, the reaction mixture was irradiated with filtered UV light for 1.5 h, whereupon complete transformation of **2** was indicated by TLC monitoring.

After adding *n*-Bu_3SnH (565 μL, 2 mmol, 3 equiv) irradiation was applied for 30 min. TLC monitoring showed the formation of **6** (R_f 0.7 in 1:1 EtOAc–petroleum ether), **3** (R_f 0.65 in 1:1 EtOAc–petroleum ether), **7** (R_f 0.48 in 1:1 EtOAc–petroleum ether), **16** (R_f 0.48 in 20:1 EtOAc–EtOH), and **12β** as the major product (R_f 0.46 in 20:1 EtOAc–EtOH). The reaction mixture was filtered through a bed of Celite, concentrated under reduced pressure, and the residue was dissolved in MeCN (30 mL). The resulting organic phase was washed with hexanes (3 × 30 mL) in order to remove the tin compounds. Then, the MeCN phase was concentrated under reduced pressure and the residue was applied to a column of silica gel developed following a gradient technique (1:1.5–1:1 EtOAc–petroleum ether then 40:1–20:1 EtOAc–EtOH) to afford the following compounds: **6** (3.5 mg, 1%), **3** (65.7 mg, 29%, no rearranged product detected by ^{1}H NMR), **7** (21.6 mg, 9%), **16** (24.7 mg, 7%), and **12β** (126.6 mg, 38%).

Compound **12β**: white solid, mp: 70–74 °C (CH_2Cl_2–cyclohexane); $[\alpha]_D^{25}$ −11° (*c* 1, acetone); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.08 (t, 1 H, $J_{4,5}$ 9.7 Hz, H-5), 4.96 (t, 1 H, $J_{5,6}$ 9.8 Hz, H-6), 4.79 (t, 1 H, $J_{3,4}$ 9.2 Hz, H-4), 4.14 (dd, 1 H, $J_{7,8a}$ 4.9, $J_{8a,8b}$ 12.3 Hz, H-8a), 4.15–3.9 (m, 5 H, H-8b, OCH_2CH_3), 3.55 (ddd, 1 H, $J_{6,7}$ 9.8, $J_{7,8b}$ 2.4 Hz, H-7), 3.41 (ddd, 1 H, $J_{2a,3}$ 2.2, $J_{2b,3}$ 9.2 Hz, H-3), 2.1–1.5 (m, 4 H, H-1a, H-1b, H-2a, H-2b), 2.02, 1.98, 1.96, 1.93 (4s, 12 H, acetyl), 1.23 (t, 6 H, $J_{CH\text{-}2,CH\text{-}3}$ 7.0 Hz, OCH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.0, 170.7, 170.0, 169.9 (C=O), 77.1 (d, $J_{C\text{-}3,P}$ 15.4 Hz, C-3), 75.8 (C-7), 74.4 (C-5), 71.6 (C-4), 68.7 (C-6), 62.4 (C-8), 61.8 (d, $^2J_{C,P}$ 6.7 Hz, OCH_2CH_3), 61.8 (d, $^2J_{C,P}$ 6.7 Hz, OCH_2CH_3), 24.7 (d, $^2J_{C\text{-}2,P}$ 3.9 Hz, C-2), 21.0 (d, $^1J_{C,P}$ 143 Hz, C-1), 21.0, 20.9, 20.84, 20.82 (4s, acetyl), 16.6 (d, 2 C, $^3J_{C,P}$ 6.2 Hz, OCH_2CH_3); ^{31}P NMR (81 MHz, $CDCl_3$): δ 31.70; MS (FAB$^+$, glycerol + LiCl): *m*/*z* 503 $[M+Li]^+$; Anal. Calcd for $C_{20}H_{33}O_{12}P$: C, 48.39; H, 6.70; P, 6.24. Found: C, 48.54; H, 6.87; P, 5.60.

Compound **16**: white solid, mp: 122 °C (CH_2Cl_2–cyclohexane); $[\alpha]_D^{25}$ +13° (*c* 1, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.66 (s, 1 H, OH), 5.48 (t, 1 H, $J_{4,5}$ 9.6 Hz, H-5), 5.07 (t, 1 H, $J_{5,6}$ 9.6 Hz, H-6), 4.88 (d, 1 H, $J_{3,4}$ 9.8 Hz, H-4), 4.29–4.24 (m, 2 H, H-7, H-8a), 4.18–4.03 (m, 5 H, H-8b, 2 OCH_2CH_3), ~1.95–1.75 (m, 2 H, H-1a, H-1b), ~1.75–1.55 (m, 2 H, H-2a, H-2b), 2.09, 2.08, 2.02, 1.97 (4s, 12 H, acetyl), 1.33 (dt, 6 H, $J_{CH\text{-}2,CH\text{-}3}$ 7.1, $^4J_{CH\text{-}3,P}$ 5.1 Hz, 2 OCH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.1, 170.6, 170.4, 170.1 (C=O), 96.4 (d, $^3J_{C\text{-}3,P}$ 6.5 Hz, C-3), 74.1 (C-4), 72.0 (C-5), 69.3 (C-6), 68.3 (C-7), 62.8 (d, $^2J_{C,P}$ 6.7 Hz, OCH_2CH_3), 62.6 (d, $^2J_{C,P}$ 6.7 Hz, OCH_2CH_3), 62.5 (C-8), 30.7 (d, $^2J_{C\text{-}2,P}$ 4 Hz, C-2), 21.2, 21.1, 21.1, 21.0 (4s, acetyl), 18.6 (d, $^1J_{C\text{-}1,P}$ 141.1 Hz, C-1), 16.8 (d, $J_{CH\text{-}3,P}$ 6.1 Hz, OCH_2CH_3), 16.7 (d, $J_{CH\text{-}3,P}$ 6.1 Hz, OCH_2CH_3); ^{31}P NMR (81 MHz, $CDCl_3$): δ 34.67; Anal. Calcd for $C_{20}H_{33}O_{13}P$: C, 46.88; H, 6.49; P, 6.04. Found: C, 46.94; H, 6.54; P, 6.03.

2,3,4,6-Tetra-O-*acetyl-1,5-anhydro*-D-*glucitol* (**3**).—To a mixture of **1** (200 mg, 0.486 mmol) and $NaBH_3CN$ (60.3 mg, 1 mmol, 2 equiv) in *tert*-butanol (8 mL) in a quartz tube (~94 mL volume, 27 mm external diameter) and under argon, thiophenol (5 μL, 0.05 mmol, 0.1 equiv) was added and the medium was irradiated with filtered UV light for 1.75 h. TLC Monitoring showed the conversion of the starting bromide (R_f 0.70) into **3**–**4** (R_f 0.65) and **7** (R_f 0.34 in 1:1 EtOAc–petroleum ether). After the mixture was concentrated under reduced pressure, the oily residue dissolved in CH_2Cl_2 (30 mL) was washed with water (3 × 30 mL). After workup, the crude product (166.4 mg) was shown by ^{1}H NMR to contain **3**, **4**, and **7** in a ~97:0.5:2.5 ratio (estimated weight of **3**–**4**: ~139 mg). Concentration of homogeneous fractions obtained from a column of chromatography eluted with 1.5:3 EtOAc–petroleum ether afforded **3** in admixture with **4** (128.3 mg, 0.386 mmol, 79%, **3**–**4** ratio: 98:2 by ^{1}H NMR), and **7** (11.1 mg, 0.032 mmol, 7%). Compound **3** crystallized as colorless crystals (126.6 mg, 0.381 mmol, 78%), mp 68–70 °C (1:3 CH_2Cl_2–petroleum ether), lit.[24] 68–69 °C; ^{1}H NMR data in agreement with Ref. 25 but not with Ref. 44; ^{13}C NMR (50 MHz, $CDCl_3$):[45] δ 170.4, 170.1, 169.5, 169.3 (C=O), 76.2 (C-5), 73.5 (C-3), 68.7 C-2), 68.2 (C-4), 66.6 (C-1), 62.0 (C-6), 20.55, 20.5 (2 C), 20.4 (acetyl).

1,3,4,6-Tetra-O-*acetyl-2-deoxy*-α-D-*arabino-hexopyranose* (**4**).—A mixture of **1** (200 mg, 0.486 mmol) and $NaBH_3CN$ (60.3 mg, 1 mmol, 2 equiv) in *tert*-butanol (8 mL) was irradiated with filtered UV light for 35 min and treated as before. The crude mixture (133.2 mg, 82%) which was shown by ^{1}H NMR to contain only **3** and **4** in a ratio <5:95 crystallized from acetone–cyclohexane to afford **4** (104.6 mg, 65%) as colorless prisms, mp 108–110 °C lit.[28] 109–110 °C; ^{13}C NMR (50 MHz, $CDCl_3$):[45] δ 170.7, 170.3, 169.7, 168.9 (C=O), 90.9 (C-1), 70.2 (C-5), 68.7 (C-4), 68.5 (C-3), 62.0 (C-6), 33.9 (C-2), 21.0, 20.9, 20.7, 20.7 (acetyl).

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