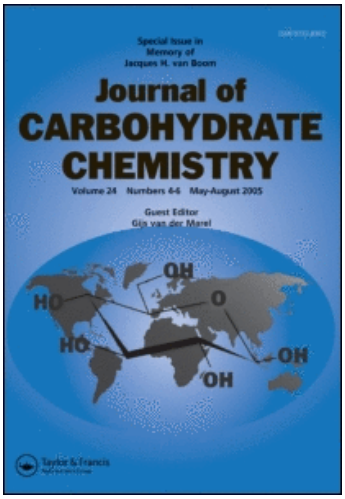

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A Novel Approach to the Synthesis of C-Glycosyl Compounds: The Wittig Rearrangement

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A NOVEL APPROACH TO THE SYNTHESIS OF C-GLYCOSYL COMPOUNDS: THE WITTIG REARRANGEMENT

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ABSTRACT

Partially protected benzyl α- and β-pyranosides undergo Wittig rearrangement reactions on treatment with strong bases in tetrahydrofuran to give hydroxymethylphenyl C-glycosyl derivatives. Two products were generally obtained and all Wittig rearrangement products retained the configuration at the migrating anomeric center. In benzene, benzyl 4,6-O-isopropylidene-β-D-glucopyranoside reacted with n-butyl lithium to give addition to the anomeric center accompanied by ring opening with loss of the aglycone. Allyl glycosides do not give Wittig rearrangement products.

INTRODUCTION

The rearrangement of an α-ethereal carbanion to the corresponding alkoxide is termed the Wittig rearrangement.[1]

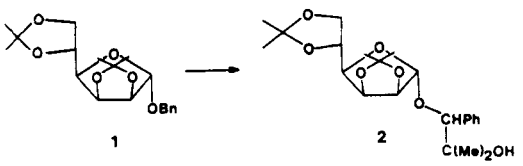
In order to form the carbanion, an anion stabilizing substituent is required. The rearrangement of simple alkyl ethers occurs rapidly at -78 °C if the stabilizing group is phenyl or vinyl but slows if more stabilization is provided. Glycosides with aglycones having O-methylene groups attached to slightly anion stabilizing groups like phenyl, vinyl or others can be prepared easily.

Thus, the Wittig rearrangement is potentially a source of novel C-glycosyl compounds.

A complication is the other reactions known to occur when protected carbohydrates are treated with strong bases. Klemer and coworkers and others have shown that acetal protected carbohydrates undergo proton abstraction followed by loss of the aldehyde or ketone to give unsaturated derivatives of various types depending on the structure and stereochemistry of the substrate[2-4]. The usefulness of the Wittig rearrangement as a source of C-glycosyl derivatives depends on the relative rates of the rearrangement as opposed to these processes. This publication reports a study of this question.

RESULTS AND DISCUSSION

A Wittig rearrangement was attempted on the anion



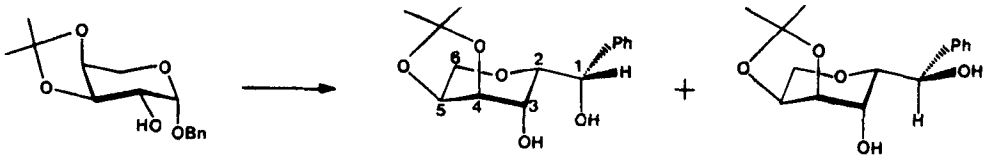
derived from benzyl 2,3:5,6-di-O-isopropylidene-α-D-mannofuranose (1) by stirring it in tetrahydrofuran at -78 °C. The only product isolated was the result of the addition of the benzyl anion to acetone released from the decomposition of 1. The anion required for the Wittig rearrangement formed but the rearrangement was slower than the other possible processes for 1.

Extension of the study to partially protected substrates proved successful. Benzyl 3,4-O-isopropylidene-β-L-arabinopyranoside (4) was prepared in good yield by isopropylidenation of benzyl β-L-arabinopyranoside with 2-methoxypropene in N,N'-dimethylformamide. Wittig rearrangement of 4 with n-butyl lithium as base in tetrahydrofuran under reflux yielded two Wittig rearrangement products (5 and (6) in the ratio of 11:8.

Table 1. ^{1}H NMR chemical shifts[a]

Compound	H-1	H-2	H-3	H-4	H-5	H-5'	H-6	H-6'	H-7	H-7'
4	4.90	3.78	4.18	4.20	3.98	3.91				
5	5.15	3.74	3.90	4.16	4.34		3.67	4.14		
6	4.88	3.70	3.75	4.18	4.34		4.09	3.50		
8	4.40	3.47	3.61	3.53	3.22		3.92	3.79		
9	5.88	3.98	4.94	5.89	3.53		3.36		3.88	3.67
10	4.78	3.51	3.59	3.47	3.37		3.14		3.75	3.53
12	4.40	3.47	3.63	3.57	3.22		3.90	3.77		
13	4.45	3.74	3.41	3.56	3.62		3.89	3.75		
14	4.77	3.40	3.56	3.81	3.33		3.90	3.90		
15	4.83	3.58	3.56	3.65	3.44		3.20		3.78	3.63
17	4.86	3.47	3.43	3.41	3.67		3.75	3.55		
18	5.19	4.07	3.96 -- 4.05				3.42 -- 3.54			
19	5.28	4.00	3.95	4.45	3.53		4.28		3.71	3.44

a. In ppm downfield from internal TMS in chloroform-d at 361 MHz.



4 5 6

Almost identical ratios of the same products were obtained from a reaction at 20 °C. The structures of 5 and 6 were established from analysis of the spectral data. ^{13}C NMR spectra of 5 and 6 indicated that they were Wittig rearrangement products because the signals of the anomeric and benzyl carbons had disappeared and signals of two additional secondary carbons bonded to oxygen had appeared.

Product stereochemistries were established from the ^{1}H NMR coupling constants. The mechanism accepted for the Wittig rearrangement is a radical cleavage-recombination process.[1,5] Thus, the configurations at the former anomeric center as well as at the new chiral center need to be assigned. With acyclic ethers, chiral migrating groups partially racemize during rearrangement.[6] The starting material (4) existed mostly in a $^{4}C_{1}$ conformation, albeit somewhat distorted, as shown by the values of $J_{2,3}$, $J_{4,5}$, $J_{4,5'}$, and $J_{5,5'}$. If inversion of configuration had occurred at the former anomeric center, the magnitudes of the corresponding

Table 2. ^{1}H NMR coupling constants of arabinopyranoside derivatives[a]

Compound	Coupling Constant (Hz)								
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5'}$	$J_{4,5}$	$J_{5,5'}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6}$
4	3.57	6.86	4.40	<1.0	1.70	13.20			
5	4.20	1.12	2.20		6.10		4.80	6.56	11.74
6	6.24	1.25	2.53		5.60		5.93	8.12	11.70

a. By first-order analysis of 361 MHz spectra.

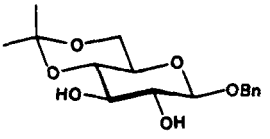
coupling constants in the spectra of 5 and 6 would be similar to those from 4, because the large hydroxyphenylmethyl group, having an overwhelming preference for an equatorial orientation, would keep the tetrahydropyran ring in the $^4C_1$ conformation. In the spectra of neither 5 nor 6 is this pattern observed. Instead, for both 5 and 6, the $J_{3,4}$ ($J_{2,3}$ in 4) values are small, consistent with diequatorial orientations and the $J_{5,6}$, values are large, consistent with diaxial orientations. Thus, both 5 and 6 adopt $^1C_4$ conformations, as would be expected if no change of configuration at the former anomeric center had taken place. The change in conformation is caused by the change in conformational preference from axial to strongly equatorial on changing from a benzyloxy group to a hydroxyphenylmethyl group at C-1 of a tetrahydropyran ring. The configurations at the new chiral center of 5 and 6 could not be established unambiguously. The names assigned are based on differences in the magnitudes of the $J_{1,2}$ values in the spectra 5 and 6 and an analysis of the relative stabilities of rotamers about the C-1--C-2 bond but must be regarded as tentative.

When the base was changed to lithium diisopropylamide, the ratio of 5 to 6 changed dramatically to 4 : 23.

Wittig rearrangements were performed on several D-glucopyranoside derivatives to evaluate the effects of having fixed and different stereochemistries. Benzyl 4,6-O-isopropylidene-β-D-glucopyranoside (8) was prepared by isopropylidenation of the unprotected glycoside (7) under kinetic conditions. Its anticipated[7] structure was established by spectral methods. The chemical shifts of the acetal C and the isopropylidene methyl carbons in the ^{13}C NMR spectra indicated that the acetal ring was six-membered.[8] Single frequency decoupling was used to assign the ^1H NMR spectrum of 8. Heteronuclear decoupling then allowed assignment of the skeletal carbons. The chemical shift of C-5 was 67.7 ppm in the spectrum of 8, 9.6 ppm upfield of its

position in the spectrum of 7. A large upfield shift is always observed for the central carbon of a 1,3-propanediol unit on acetal formation[9] and its observation here confirms the structure of 8.

Refluxing 8 in tetrahydrofuran with n-butyl lithium again gave two products, 9 (isolated as a peracetate) and 10, in the ratio of 16 to 9, readily shown to be the results of Wittig rearrangements from the appearances of their ^{13}C NMR spectra. The large $J_{2,3}$ value in the ^{1}H NMR spectra of 9 and 10 demonstrated that the configurations at the anomeric



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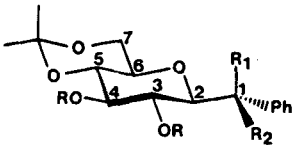
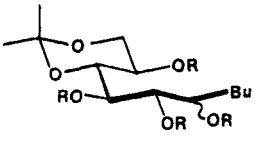


9 R = Ac R_1 = OAc R_2 = H

10 R = R_1 = H R_2 = OH



II R = H IIa R = Ac

centers had been retained. The configurations at the new chiral centers can be established unambiguously in this case. Figure 1 shows Newman projections of the three rotamers about the C-1--C-2 bond of the two possible epimers about C-1. Of the six rotamers, Ic and IIc will be of considerably higher energy because they have syn-axial relationships between the phenyl group and O-2. Thus, the populated rotamers for configuration II both have H-1 and H-2 gauche and a small value of $J_{1,2}$ would be expected. For I, both Ia, with a syn-axial

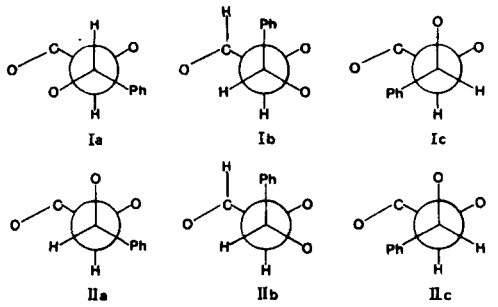


FIG. 1. Rotamers about the C-1--C-2 bond of 9 and 10

Table 3. ^{13}C NMR chemical shifts[a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	Benzyl $-OCH_2$
3[b]	99.0	68.8	68.8	68.3	63.3			69.2
4[b]	97.0	70.0	76.0	73.0	60.0			69.8
5[b]	66.2	75.9	70.1	75.4	74.3	66.4		
6[b]	67.2	78.0	69.4	75.2	74.4	67.4		
7[c]	102.7	74.5	77.3	71.4	77.3	62.0		72.8
8[b]	102.9	75.0	73.4	73.4	67.7	60.2		72.2
9[b]	73.8	79.2	76.2	69.3	71.1	70.7	61.8	
10[b]	73.0	81.0	73.0	75.8	75.7	70.9	61.9	
12[b]	102.4	74.5	73.5	72.5	67.4	64.4		71.1
13[b]	103.6	70.1	80.2	73.9	75.4	62.8		72.3
14[b]	101.0	76.2	80.4	69.3	77.6	61.8		71.0
15[b]	72.1	81.0	76.3	75.7	75.4	71.2	61.3	
16[c]	97.9	71.9	73.3	70.3	73.0	61.0		67.8
17[b]	97.4	72.2	72.3	74.9	69.9	60.5		69.9
18[b]	72.7	77.2	72.9	73.1	73.9	66.6	61.6	
19[b]	72.1	78.8	73.0	73.9	73.6	67.7	62.1	

a. In ppm downfield from internal TMS. b. In chloroform-d at 90.8 MHz. c. In dimethyl sulfoxide-d_6 at 20 MHz.

O--O interaction and Ib, with a syn-axial H--phenyl interaction would be populated significantly and a value intermediate between those expected for anti and gauche relationships should be observed. The measured values of 2.58 and 5.68 Hz confirm these expectations and lead to the configurations assigned.

Performing the reaction on 8 in refluxing benzene resulted in a small amount of the Wittig rearrangement product 10, but the major product (11) (32%) resulted from removal of the benzyl group, cleavage of the pyranose ring, and addition of a n-butyl group. The gross structure of 11 was established from the spectral data of it and its peracetate (11a); the configuration of the new chiral center, C-6, remains unassigned. The ^{13}C NMR spectrum of 11 showed that a six-membered isopropylidene ring remained (signals of the acetal C at 99.2 ppm and two methyl C at 19.9 and 28.2 ppm), that no phenyl group or anomeric carbons were present, but that a butyl group had been added (signals of three methylene groups at 22.7, 28.0, and 33.1 ppm, plus a methyl group at 14.0 ppm). Cleavage of the pyranose ring was demonstrated by formation of a tetraacetate (11a) rather than a triacetate on acetylation. It was confirmed by analysis of the ^{1}H NMR spectrum of 11a; the coupling constants $J_{1,2}$, and $J_{2,3}$ were large (7.80, 9.25 Hz) as expected between vicinal anti hydrogen atoms in a six-membered ring. The magnitudes of $J_{3,4}$ and $J_{4,5}$ (2.62 and 5.75 Hz) were not consistent with the vicinal anti relationships required if the pyranose ring or a 2,6-anhydro ring had remained.

The mechanism of formation of 11 is probably analogous to that observed for cleavage of acetal rings on refluxing in benzene or toluene with Grignard reagents.[11,12] The mechanism is thought to involve a carbocation at the former acetal carbon.[11,12] As far as we are aware, cleavage of furanose or pyranose rings with loss of the aglycone has not been previously observed. Methyl glycosides do not cleave in this way, although they do anomerize and ring open.[12] With

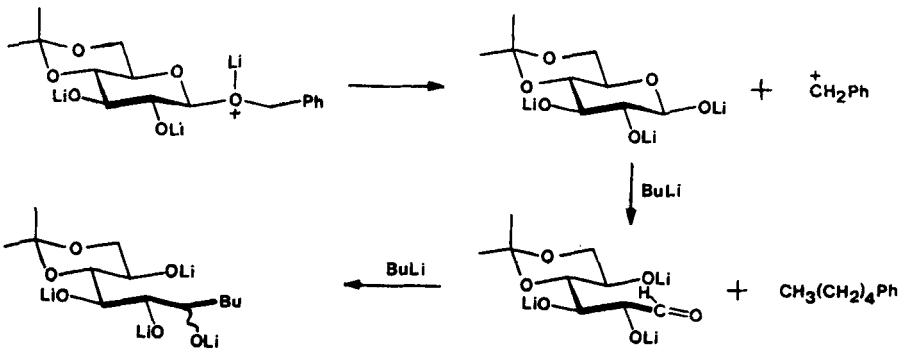
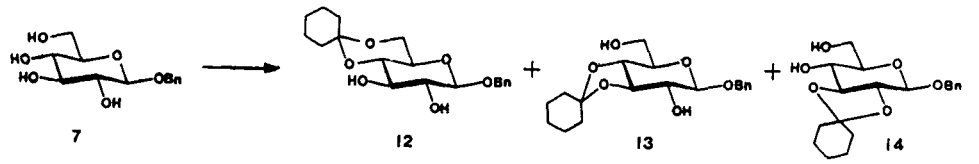


FIG. 2. Pathway for formation of a C-glycosyl derivative with ring opening.

benzyl glycosides, an alternative site for carbocation formation is possible and the reaction pathway outlined in Figure 2 is preferred to cleavage of the acetal ring. The direction of the reaction shifts sharply on change of solvent from an ether to benzene because the lithium cation now complexes only with substrate oxygens. It is noteworthy that only one of the two possible epimers at C-6 was obtained.

Kinetic cyclohexylidenation of 7 gave one major product, benzyl 4,6-O-cyclohexylidene-β-D-glucopyranoside (12) (40 %) and two unexpected minor products, the 3,4- (13) (2 %) and 2,3- (14) (4 %) isomers. The structure of 12 was assigned exactly as for 8. The chemical shifts of the

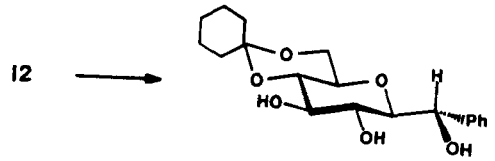


acetal carbons (113.4 and 112.5 ppm, respectively) and the small chemical shift differences between the cyclohexyl - carbons (0.3 ppm for both) in the ^{13}C NMR spectra of 13 and 14 indicated that both contained 1,3-dioxolane rings.[9] Only

two structures are possible, the 2,3- and 3,4-O-cyclohexylidene derivatives. Assignments were made by consideration of the 361 MHz ^{1}H NMR spectra using the smaller value of $J_{1,2}$[10] as compared to $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ and the observation that the signals of hydrogens geminal to OH groups were broad in chloroform-d but sharp when water-d_2 was added. Comparison of the ^{13}C NMR chemical shifts of C-2, C-3, and C-4 (assigned by heteronuclear decoupling) of 13 and 14 with those of 7 confirmed the structures.[9]

Treatment of 12 with n-butyl lithium in tetrahydrofuran at reflux gave one major Wittig rearrangement product (15) with the same stereochemistry as the minor Wittig product (10) from the rearrangement of 8.

Benzyl α-D-glucopyanoside (16) was prepared from the α,β-mixture[13] by peracetylation, enrichment in the α-anomer by



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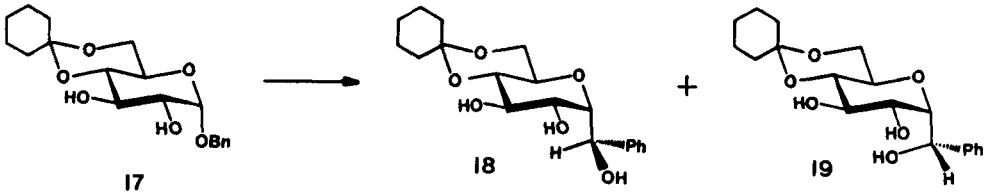

17 18 19

the method of Piel and Purves[14], and deacetylation. Kinetic cyclohexylidenation of 16 yielded its 4,6-O-cyclohexylidene

Table 4. ^{1}H NMR Coupling Constants of D-glucopyranoside derivatives[a]

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	$J_{6,7}$	$J_{6,7'}$	$J_{7,7'}$
8	7.80	8.42	8.33	9.2	5.40	10.10	10.75			
9	2.58	9.80	8.99	10.46	9.91			5.23	10.21	10.65
10	5.68	9.23	9.23	9.19	9.30			5.35	9.83	10.54
12	7.69	8.01	8.81	9.32	5.46	9.14	10.86			
13	6.86	9.11	9.22	9.13	2.83	5.59	11.86			
14	7.76	9.44	9.52	9.44	4.30	3.26	11.71			
15	5.57	9.16	9.57	9.69	9.17			5.43	9.17	10.70
17	3.78	10.30	9.28	9.45	5.92	9.32	10.40			
18	9.01	5.16								
19	2.29	6.97	8.72	9.68	9.51			5.46	9.19	10.41

a. By first-order analysis.

derivative (17). The reaction of 17 with n-butyl lithium in tetrahydrofuran at reflux gave two Wittig rearrangement products 18 and 19 in yields of 21 and 16%, respectively. Because of the large steric effect of an axial hydroxyphenylmethyl group, this reaction is the most likely of all Wittig rearrangements studied to give products that had not retained the configuration at the former anomeric center, now C-2. Both products could not have inverted configurations because neither was identical to 15 and the similarity of the ^{13}C chemical shifts of 18 and 19 suggests that both have the same configuration at C-2. The 361 MHz ^{1}H NMR spectrum of 19 could be fully analysed. The product of inversion of configuration at C-2 would have a value of $J_{2,3}$ of about 9 -- 10 Hz, as observed in the spectra of 9, 10 and 15. The $J_{2,3}$ values in the spectra of 18 and 19, were 5.16 and 6.97 Hz, respectively, much smaller than expected if inversion had occured, but larger than $J_{1,2}$ in 17. Presumably, there is considerable distortion of this part of the tetrahydropyran ring.

The large differences between the values of $J_{1,2}$ for 18 and 19, 9.01 and 2.29 Hz, respectively, allowed ready assignment of the configurations at the new chiral center by consideration of the relative stabilities of rotamers about the C-1--C-2 bond (Figure 3). For configuration III, rotamer a is destabilized by a syn-axial O--O interaction, but the other two are considerably more destabilized. A large preference for IIIa would be expected and $J_{1,2}$ for III should be large, about 9 Hz. In contrast, IV should be present mainly in two

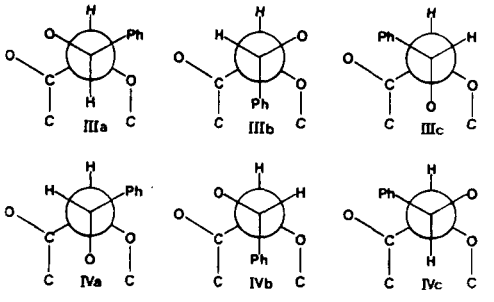

FIG. 3. Rotamers about the C-1--C-2 bond of 18 and 19.

rotamers, IVa and IVc, with H-1 and H-2 anti and gauche, respectively. The value of $J_{1,2}$ should lie between 2 and 9 Hz. The values obtained show that 18 has configuration III, and thus 19 has to have configuration IV. The larger value of $J_{2,3}$ for 19 suggesting a more distorted ring is in agreement with the assessment that its populated rotamers are more strained than those of 18.

Attempted Wittig rearrangements on allyl 3,4-O-isopropylidene-β-L-arabinopyranoside under a variety of conditions did not yield the products of Wittig rearrangements.

CONCLUSIONS

The α-benzyl anion required for the Wittig rearrangement is formed readily at room temperature or below with lithium diisopropylamide on monoanions like the one derived from 4 or with n-butyl lithium on dianions like those derived from 8, 12, or 17. The Wittig rearrangement of the carbohydrate derived benzyl anions is much slower than those of simple alkyl anions so that vigorous conditions are required to make the reactions proceed. The vigorous reaction conditions result in proton abstraction at other sites on the carbohydrate rings and lower yields.

The products obtained from the migration of chiral groups always retained the starting stereochemistry unlike the products of Wittig rearrangements of acyclic chiral molecules.[6] Presumably, the large size of the cyclic anomeric radical which is also a mono or dianion complexed to lithium and then to solvent molecules, stops movement of the ketyl radical anion from the leaving face to the other face of the anomeric radical or independent rotation of the anomeric radical. The new chiral centers were produced as mixtures of epimers with varying degrees of selectivity.

EXPERIMENTAL

General Methods. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Opti-

cal rotations were measured on a Perkin-Elmer 141 polarimeter. ^{1}H NMR spectra were recorded at 361 MHz on a Nicolet NT-360 NB spectrometer on solutions in chloroform-d containing tetramethylsilane as reference. ^{13}C NMR spectra were measured at 20 MHz or at 90.8 MHz on Varian CFT-20 or Nicolet NT-360 NB spectrometers, respectively. Most mass spectra were recorded on a CEC 21-104 mass spectrometer with 70-eV ionizing voltage and an inlet temperature of 150 °C; exact masses were determined on a Dupont CEC 21-110B mass spectrometer. Microanalyses were performed by the Canadian Microanalytical Service, Ltd., Vancouver, B.C. Bath temperatures for reactions at 0 °C were controlled with a Haake FK circulating bath. TLC was performed on 0.2-mm thick Merck Silica Gel 60F-254 aluminum plates cut to be approximately 7 cm long. Pet ether refers to petrolium ether (30-60 °C). Solvents used for chromatography were mixtures of: pet ether and ethyl acetate, a, 3:2; b, 2:1; c, 1:1; d, 1:2; e, 1:3; pet ether and diethyl ether, f, 1:1; g, 2:3; toluene and ethyl acetate, h, 1:3; j, 1:7; chloroform and isopropanol, k, 10:1, ethyl acetate and methanol, l, 25:4; hexane and diethyl ether, m, 1:5. Glassware for dry reactions was dried overnight in the oven at 120 °C, cooled in a stream of dry nitrogen, assembled quickly, then flushed with argon. Tetrahydrofuran (THF) was distilled over lithium aluminium hydride in an argon atmosphere directly into the reaction flask. N,N,N',N'-tetramethylethylenediamine (TMEDA) and diisopropylamine were dried over potassium hydroxide pellets overnight, distilled and stored under argon at 5 °C. N,N'-Dimethylformamide (DMF) was purified by distillation from calcium hydride. Dry reagents were transferred by syringe when required. p-Toluenesulfonic acid was anhydrous, obtained by dehydration of the commercial monohydrate for 5h at 56 °C under vacuum (0.5 torr) in the presence of phosphorus pentoxide. n-Butyllithium (2.7 M in n-hexane) was purchased from Aldrich Chemical Company and standardized with 2,5-dimethoxybenzyl alcohol prior to use.[15] Other starting materials were dried overnight in a drying pistol at 55 °C

and 0.5 torr. In the workup of reactions, solutions in organic solvents were dried with anhydrous magnesium sulfate.

Attempted Wittig Rearrangement of Benzyl 2,3:5,6-di-O-isopropylidene- α -D-mannofuranoside (1). To a solution of 1[16] (0.700 g, 2 mM) and TMEDA (0.348 g, 3 mM) in dry THF (10 mL) at -78 °C under argon was slowly added a solution of n-butyllithium (2.70 mL, 3 mM, 1.11 M). The reddish brown solution obtained was stirred for 3 h at -78 °C. Methanol (10 mL) was added to the reaction mixture, then water (25 mL). The reaction mixture was extracted with dichloromethane (3 x 25 mL), and the combined dichloromethane extracts were washed with dilute hydrochloric acid (25 mL, 2%), and water (2 x 25 mL), dried, filtered and concentrated to a red syrup (0.371 g, 53%). The syrup, a complex mixture, (R_fs 0.86, 0.53, 0.48, 0.41, 0.23, and 0.16 in solvent c), was fractionated on a column of silica gel (20 g) using solvent c as the eluent into five fractions, benzaldehyde (0.085 g, R_f 0.86), a mixture (0.031 g, R_fs 0.53, 0.48, 0.41), A (.086 g, R_f 0.23), B (0.028 g, R_f 0.16) and C (0.034 g, R_f 0.09).

Fraction A was a syrup, 1'-(2'-hydroxy-2'-methyl-1'-phenyl)propyl 2,3:5,6-di-O-isopropylidene- α -D-mannofuranoside (2), $[\alpha]_D^{27}$ +94.4° (c 3.80, chloroform); ^{1}H NMR δ 1.11, 1.19, 1.31, 1.46 (4 s, 3 H each, isopropylidene methyl groups), 1.39 (s, 6 H, propyl methyls), 2.05 (br s, 1 H, exchanged with D_2O, OH), 4.04 (dd, 1 H, J 6,6'= 8.66, 5,6'= 4.52 Hz, H-6'), 4.05 (t, 1 H, J=4.52 Hz, H-4), 4.13 (dd, 1 H, $J_{5,6}$=6.24 Hz, H-6), 4.40 (complex m, H-5), 4.43 (s, 1 H, H-1'), 4.71 (d, 1 H, $J_{2,5}$=5.91 Hz, H-2), 4.84 (s, 1 H, H-1), 4.86 (dd, 1 H, $J_{3,4}$=3.56 Hz, H-3); ^{13}C NMR δ 24.6, 25.3, 25.6, 25.9, 26.4, 26.9 (6s, Me C), 72.4 (s, C-2'), 84.2 (d, C-1'), 109.3, 112.9 (2s, acetal C); m/z: 393 (37), 351 (5), 350 (25), 201 (14), 186 (12), 185 (36), 165 (19), 149 (45), 143 (16), 127 (20), 107 (41), 101 (57), 91 (20), 85 (21), 69 (25), 59 (48), 43 (100). Exact mass. Calcd for $C_{21}H_{29}O_7$: 393.1914. Found: 393.1906.

Benzyl 3,4-O-isopropylidene- β -L-arabinopyranoside (4). Benzyl β -L-arabinopyranoside (3)[17] (5.00 g, 20.83 mM), 2-

methoxypropene (2.10 g, 29.16 mM) and p-toluenesulfonic acid (120 mg) were stirred with exclusion of moisture at room temperature in DMF (40 mL) for 2 h. The mixture was then poured into a solution of sodium hydrogencarbonate (2% w/v, 100 mL). The mixture was extracted with diethyl ether (4 x 100 mL) and the combined ether extracts washed with water (2 x 100 mL), dried and evaporated to a syrup (5.58 g, 96%, R_f 0.52 in solvent a) which solidified to a white mass. Recrystallization from ethanol gave the title compound (4) (4.86 g, 84%), mp 57-58 °C (lit.[18] 55-58 °C); $[\alpha]_D^{22}$ +201.8° (c 1.927, ethanol) (lit.[18] (D-isomer) -209°; ^{13}C NMR δ 25.9, 27.9 (q, Me C), 109.3 (s, acetal C), 128.1, 128.6, 137.2 (Ph C), for remainder, see Table 3.

Wittig Rearrangement of 4. To a stirred solution of 4 (0.560 g, 2 mM) and TMEDA (0.696 g, 6 mM) in dry THF (10 mL) at room temperature under argon was slowly added n-butyllithium (6 mM, 5.40 mL, 1.11 M). The resultant reddish-brown reaction mixture was refluxed for 20 h, cooled, quenched with methanol (20 mL), and worked up using the standard method to give a red syrup (0.336 g, 59%). The syrup was fractionated on a solumn of silica gel (20 g) using solvent a as eluent into three fractions, starting material (0.045 g, 8%), A (0.062 g, 11%, solid) and B (0.045 g, 8%, syrup) (R_fs 0.62, 0.40, 0.25 in solvent c).

Fraction A was recrystallized twice from dichloromethane-pet ether to give fine colorless needles of 2,6-anhydro-1-phenyl-L-glycero-L-ido-hexitol (5), mp 169-170 °C; $[\alpha]_D^{25}$ -10.3° (c 1.55, chloroform); ^{1}H NMR δ 1.31, 1.45 (2 s, 3 H each, isopropylidene methyls), 3.29 (d, 1 H, $J_{7,OH-1}$=3.35 Hz, exchanged with D_2O, OH-1), 4.14 (d, 1 H, $J_{3,OH-2}$=1.98 Hz, exchanged with D_2O, OH-3), 7.38 (complex m, 5H, phenyl), for remainder, see Tables 1 and 2; ^{13}C NMR δ 25.3, 27.6 (q, Me C), 109.2 (s, acetal C), 125.7, 128.0, 128.6, 138.6 (Ph C), for remainder, see Table 3; m/z 265 (10), 156 (76), 155 (31), 141 (83), 107 (37), 105 (28), 91 (40), 85 (26), 81 (100), 77 (30), 69 (22), 59 (83), 57 (42), 43 (79). Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.18; H, 7.21.

Fraction B was a syrup, 2,6-anhydro-1-phenyl-L-glycero-L-gulo-hexitol (6); $[\alpha]_D^{25}$ +240.3° (c 2.04, chloroform); ^{1}H NMR δ 1.31, 1.45 (2 s, 3 H each, Me), 3.08 (d, 1 H, J 6 Hz, exchanged with D_2O, OH-3), 3.15 (d, 1 H, $J_{1,OH-1}$=2.9 Hz, exchanged with D_2O, OH-1), for remainder, see Tables 1 and 2; ^{13}C NMR δ 25.8, 27.9 (q, Me C), 109.6 (s, acetal C), 126.9, 128.0, 128.5, 139.5 (Ph C), for remainder, see Table 3; m/z: 265 (36, M - ·Me), 156 (91), 155 (44), 140 (100), 131 (47), 107 (39), 105 (27), 91 (76), 59 (55). Exact mass. Calcd for $C_{14}H_{17}O_5$: 265.107. Found: 265.107.

With Lithium Diisopropylamide. To a stirred solution of compound 42b (0.560 g, 2 mM) in dry THF (10 mL) at room temperature under argon was added dry diisopropylamine (0.606 g, 6 mM). A solution of n-butyllithium (3 mL, 5 mM, 2.0 M) was added slowly. The brownish-red reaction mixture was stirred at room temperature for 72 h. Standard work up gave a red syrup (0.333 g, 59%) which was chromatographed on a column of silica gel (10 g) using solvent a as eluent to give compounds 5 (0.025 g, 4%, solid) and 6 (0.129 g, 23%, syrup), (R_fs 0.40 and 0.25 in solvent c).

Benzyl 4,6-O-isopropylidene-β-D-glucopyranoside (8). To the solution of dry benzyl-β-D-glucopyranoside (7)[14,19] (5.02 g, 18.5 mM) and 2-methoxypropene (1.598 g, 22.2 mM) in anhydrous DMF (40 mL) at 2 °C was added p-toluenesulfonic acid (120 mg). The homogeneous reaction mixture was kept at 2 °C with the exclusion of moisture for 16 h, then poured into a solution of sodium hydrogencarbonate (2% w/v, 100 mL). This mixture was extracted with diethyl ether (4 x 100 mL). The combined ether extracts were washed with water (2 x 100 mL), dried and concentrated to a light yellow syrup (4.30 g, 75%, R_f 0.58 in ethyl acetate). The product was purified by column chromatography on silica gel (55 g) using solvent c as eluent to give the title compound (8) (3.40 g, 59%), $[\alpha]_D^{25}$ -67.8° (c 1.33, chloroform); ^{1}H NMR δ 1.01 (br s, 1 H, exchanged with D_2O, OH), 2.46 (br d, 1 H, J-3.5 Hz, OH), 1.42, 1.45 (2 s, 3 H each, isopropylidene methyls), 4.60, 4.88 (AB q, 2 H, J=11.61 Hz, benzylic H), 7.33 (com-

plex m, 5 H, phenyl), for remainder, see tables 1 and 4; ^{13}C NMR δ 19.5, 29.4 (q, Me C), 99.5 (s, acetal C), 127.3, 128.7, 129.1, 136.7 (Ph C), for remainder, see Table 3; m/z 295 (M - •Me), 295 (5, M-•CH_2Ph), 161 (7), 143 (13), 101 (15), 91 (100, $^{+}CH_2$Ph), 59 (28), 57 (14), 43 (17). Exact mass. Calcd for $C_{15}H_{19}O_6$: 295.118. Found: 295.119.

Wittig Rearrangement of 8. To a stirred solution of 8 (0.620 g, 2 mM) and dry TMEDA (1.044 g, 9 mM) in dry THF (15 mL) at room temperature under argon was slowly added a solution of n-butyllithium (4.5 mL, 9 mM, 2.0 M). The reaction mixture was refluxed for 9 h, cooled, then quenched with aqueous ammonium chloride (0.011 M, 1 mL) and concentrated. The residue was taken up in dichloro-methane (100 mL). The mixture was filtered and the filtrate concentrated to a syrupy mixture (R_fs 0.85, 0.74, 0.32 and 0.15 in solvent d). The syrup was fractionated by column chromatography on silica gel (35 g) into starting material (0.033 g, 5%), and fractions A (0.096 g, 16%), and B (0.052 g, 9%).

Fraction A (0.030 g), acetic anhydride (1 mL) and pyridine (1.2 mL) were kept at 0 °C for 1 h, 12 h at room temperature, then poured into ice-water (20 mL). The mixture was extracted with dichloromethane (3 x 20 mL). The combined extracts were washed with a solution of sodium hydrogencarbonate, ice-cold dilute sulfuric acid, and water then dried over anhydrous magnesium sulfate, filtered and concentrated to give a white solid (0.035 g, 83%). Recrystallization from dichloromethane - pet ether gave very tiny colorless crystals of 1,3,4-tri-O-acetyl-2,6-anhydro-5,7-O-isopropylidene-1-phenyl-D-erythro-L-galacto-heptitol (9), mp 123-124 °C; $[\alpha]_D^{27}$ -36.9° (c, 1.21 chloroform); ^1H NMR δ 1.36, 1.41 (2 s, 6 H, isopropylidene methyl groups), 1.82, 2.00, 2.14 (3 s, 12 H, $OCOCH_3$), 7.32 (m, 5 H, phenyl), for remainder, see Tables 1 and 4; ^{13}C NMR δ 20.35, 20.38, 20.5, 20.7 (q, isopropylidene and acetyl Me C), 28.7 (q, Me C), 127.2, 127.5, 128.0, 135.1 (Ph C), 169.5, 169.5, 170.2 (CO C), for remainder, see Table 3; m/z 421 (11, M-•CH_3), 376 (1, M-CH_3CO_2H), 316 (1), 287 (29, M-•CHPhOAc), 229 (5), 227 (6),

200 (4), 169 (17), 127 (10), 111 (11), 105 (22, $^{+}$COPh), 43 (100). Exact mass. Calcd for $C_{21}H_{25}O_9$: 421.150. Found: 421.149.

Fraction B was a syrup, 2,6-anhydro-5,7-O-isopropylidene-1-phenyl-D-erythro-L-tallo-heptitol (10), $[\alpha]_D^{26}$ -10.1° (c 2.07, chloroform); ^{1}H NMR δ 1.36, 1.42 (2 s, 6 H, isopropylidene methyls), 2.85 (br d, 1 H, J = 8.0 Hz, exchanged with D_2O, OH), 3.20 (d, 1 H, J = 6.4 Hz, exchanged with D_2O, OH), 4.01 (br s, 1 H, exchanged with D_2O, OH), 7.33 (complex m, 5 H, phenyl), for remainder, see Tables 1 and 4; ^{13}C NMR δ 19.0, 28.9 (q, Me C), 99.5 (s, acetal C), 127.5, 128.6, 128.9, 140.6 (Ph C), for remainder, see Table 3. Exact mass. Calcd for $C_{15}H_{19}O_6$: 295.118. Found: 295.119.

In Benzene. The reaction was repeated exactly as before except that THF was replaced by dry benzene and refluxed for 8 h. The reaction mixture was quenched with aqueous ammonium chloride (0.011 M, 1 mL) then concentrated. The residue was taken up in dichloromethane (100 mL). The resulting mixture was filtered and the filtrate concentrated to a syrup. Column chromatography of the product on silica gel (35 g) using solvent e as eluent gave three major fractions, compounds 8 (0.079 g, 4%), 10 (0.037 g, 2%), and a new compound (11) (0.177 g, 32%, solid) (R_fs 0.51, 0.32, and 0.21 in solvent e).

Compound 11 was crystallized twice from dichloromethane-pet ether to give fine colorless needles of 7,8,9,10-tetradeoxy-D- or -L-glycero-D-gulo-1,3-O-isopropylidene-decitol (11), mp 103-104 °C; $[\alpha]_D^{25}$ -28.1° (c 1.25, chloroform); ^{1}H NMR δ 0.92 (t, 3 H, J = 6.7 Hz, CH_3), 1.25 -1.48 (m, 4 H, H-8,8',9,9'), 1.39, 1.50 (2 s, 3 H each, isopropylidene Me), 1.70 (complex m, 2H, H-7,7'), 3.50 - 4.14 (complex m); ^{13}C NMR δ14.0 (q, C-10), 19.9 (q, Me C), 22.7 (t, C-9), 28.0 (t, C-8), 28.2 (q, Me C), 33.1 (t, C-7), 63.0 (t, C-1), 64.6 (d, C-2), 68.6, 73.1, 77.1, 77.4 (4d, C-3, C-4, C-5, C-6), 99.2 (s, acetal C); m/z 263 (3, M-CH_3)$^+$, 245 (2, M-CH_3-H_2O), 221 (0.5, M-C_4H_9), 161 (1), 131 (44), 117 (6), 116 (7), 115 (5), 103 (24), 101 (24), 100 (2), 99 (10), 73

(58), 59 (100), 57 (13), 43 (27), 41 (12). Anal. Calcd for $C_{13}H_{26}O_6$: C, 56.10; H, 9.41. Found: C, 55.97, H, 9.18.

Compound 11 (0.020 g, 0.072 mM), acetic anhydride (0.5 mL) and pyridine (0.6 mL) were kept at 0 °C for 1 h, 12 h at room temperature, then poured into ice-cold water (20 mL). Workup as previously gave a syrup, 2,4,5,6-tetra-O-acetyl-7,8,9,10-tetradeoxy-D or L-glycero-D-gulo-1,3-O-isopropylidenedecitol (11a), (0.028 g, 85%), $[\alpha]_D^{27}$ - 22.4° (c 1.33, chloroform), ^{1}H NMR δ 0.90 (t, 3 H, J = 6.7 Hz, CH_3), 1.24 - 1.39 (complex m, 4 H, H-8,8',9,9'), 1.41, 1.49 (2 s, 6 H, 2 Me), 1.74 (complex m, 2H, H-7,7'), 2.02, 2.05, 2.07, 2.09 (4 s, 12 H, $COCH_3$), 3.62 (dd, 1 H, $J_{1,1'}$ = 11.6 Hz, $J_{1,2}$ = 7.8 Hz, H-1), 3.98 (dd, 1 H, $J_{2,3}$ = 9.25 Hz, $J_{3,4}$ = 2.62 Hz, H-3), 3.99 (dd, 1 H, $J_{1',2}$ = 5.48 Hz, H-1'), 4.6 (ddd, 1 H, H-2), 5.02 (ddd, $J_{6,7}$ = 9.6 Hz, $J_{6,7'}$ = 3.2 Hz, $J_{5,6}$ = 4.5 Hz, H-6), 5.30 (dd, 1 H, $J_{3,4}$ = 2.70 Hz, $J_{4,5}$ = 5.75 Hz, H-4), 5.35 (dd, 1 H, $J_{5,6}$ = 4.6 Hz, H-5).

Benzyl 4,6-Cyclohexylidene-β-D-glucopyranoside (12). To a solution of dry benzyl β-D-glucopyranoside (7) (3.00 g, 11.1 mM), 1-ethoxycyclohexene[20] (2.79 g, 22.2 mM) and anhydrous calcium sulfate (3 g) in DMF (40 mL) at 4 °C was added p-toluenesulfonic acid (10 mg). The reaction mixture was kept at 4 °C with the exclusion of moisture for 48 h. Anhydrous sodium carbonate (5 g) was added and the reaction mixture was magnetically stirred in an ice-bath for 1 h. Chloroform (100 mL) was added to the product mixture which was kept at 5 °C for 12h. The mixture was filtered and the filtrate concentrated to a yellowish syrup (3.40 g, 88%). The crude product was fractionated on a column of silica gel (135 g) using solvent d as eluent into three fractions, A (0.79 g, 2%, R_f 0.67 in solvent d), B (1.54 g, 40%, R_f 0.50), and C (0.150 g, 4%, R_f 0.35).

Fraction A was a syrup, benzyl 3,4-O-cyclohexylidene- β -D-glucopyranoside (13), $[\alpha]_D^{25}$ - 40.0° (c 1.70, chloroform); ^{1}H NMR δ 1.40, 1.98 (2 br s, 2 H, exchanged with D_2O, 2-OH), 1.56-1.73 (complex m, 10 H, cyclohexyl group), 466 (d, 1 H, J=11.66 Hz, benzylic H), 4.92 (d, 1 H, benzylic H), 7.36

(complex m, 5 H, phenyl), for remainder, see Tables 1 and 4; ^{13}C NMR δ 36.0, 36.3, 23.6, 23.6, 24.9 (cyclohexyl C), 113.4 (acetal C), 128.2, 128.5, 136.8 (Ph C), for remainder, see Table 3; m/z 350 (20, M^+), 307 (5), 259 (1), 200 (2), 161 (8), 142 (10), 99 (17), 91 (100, $^+CH_2Ph$), 55 (10). Exact mass. Calcd for $C_{19}H_{26}O_6$: 350.173. Found: 350.174.

Fraction B crystallized on standing at room temperature and was recrystallized from dichloromethane-pet ether to give colorless crystals of the title compound (12), mp 102-103 °C; $[\alpha]_D^{25}$ -66.5° (c 1.51, chloroform); ^1H NMR δ 1.34-1.61 (complex m, 10 H, cyclohexyl group), 1.82, 1.97 (2 br s, exchanged with D_2O, 2 OH), 4.40 (d, 1 H, J = 11.68 Hz, benzylic H), 4.87 (d, 1 H, benzylic H), 7.35 (complex m, 5 H, phenyl), for remainder, see Tables 1 and 4; ^{13}C NMR δ 37.8, 27.8, 25.6, 22.8, 22.5 (cyclohexyl C), 99.9 (acetal C), 127.7, 128.1, 128.4, 137.2 (Ph C), for remainder, see Table 3; m/z 350 (22, M^+), 307 (10), 259 (4), 161 (5), 143 (12), 99 (18), 92 (17), 91 (100, $^+CH_2Ph$), 70 (10), 56 (12). Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48. Found: C, 64.79; H, 7.32. Exact mass. Calcd for $C_{19}H_{26}O_6$: 350.173. Found: 350.173.

Fraction C, a solid, was recrystallized twice from dichloromethane-pet ether to give fine colorless needles of benzyl 2,3-O-cyclohexylidene-β-D-glucopyranoside (14), mp 159-160 °C; $[\alpha]_D^{25}$ -40.7° (c 1.09, chloroform); ^1H NMR δ 1.35-1.75 (complex m, 10 H, cyclohexyl group), 2.10, 2.88 (2 br s, 2 H, exchanged with D_2O, 2 OH), 4.75 (d, 1 H, J = 12.04 Hz, benzylic H), 4.88 (d, 1 H, benzylic H), 7.40 (complex m, 5 H, phenyl), for remainder, see Tables 1 and 4; ^{13}C NMR δ 36.2, 35.9, 23.7, 23.6, 24.9 (cyclohexyl C), 112.5 (acetal C), 128.4, 127.9, 137.1 (Ph C), for remainder, see Table 3; m/z 350 (4, M^+), 307 (0.2), 259 (1, $M-{}^{\cdot}CH_2Ph$), 200 (1.6), 199 (4), 161 (4, $259-C_6H_{10}O$), 99 (17, $C_6H_{10}O^+H$), 92 (11), 91 (100, $^+CH_2Ph$), 55 (13). Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.43. Found: C, 64.99; H, 7.32.

Wittig Rearrangement of 12. To a stirred solution of 12 (1.00 g, 2.84 mM) and dry TMEDA (1.482 g, 12.78 mM) in dry

THF (15 mL) under argon was slowly added a solution of n-butyllithium (6.40 mL, 12.78 mM, 2.0 M). The reaction mixture was refluxed 21 h, cooled and quenched with aqueous ammonium chloride (3.06 M, 5 mL). The solvent was removed and the residue was taken up in dichloromethane (150 mL). The mixture was filtered and the filtrate concentrated to a red syrup, a mixture (R_fs 0.98, 0.85, 0.75, 0.55, 0.35, and 0.23 in solvent h). Column chromatography on silica gel (50 g) using solvent h as eluent gave five fractions, A (0.026 g, red syrup), B (0.042 g, mixture), starting material (0.032 g, 3%), D (0.154 g, 15%), and E (0.006 g, 1%).

Fraction D was a syrup, 2,6-anhydro-5,7-O-cyclohexylidene-1-phenyl-D-erythro-L-tallo-heptitol, (15), $[\alpha]_D^{26}$ -3.5° (c 3.61, chloroform); ^{1}H NMR δ 1.35-1.60 (complex m, 10 H, cyclohexyl group), 2.68, 3.12 (2 br s, 1 H each, exchanged with D_2O, 2 OH), 2.97 (br d, 1 H, J = 2.88 Hz, exchanged with D_2O, OH-1), 7.35 (complex m, 5 H, phenyl), for remainder, see Tables 1 and 4; ^{13}C NMR δ 37.8, 27.7, 25.5, 22.7, 22.5 (cyclohexyl C), 99.8 (acetal C), 127.1, 128.1, 128.3, 136.0 (Ph C), for remainder, see Table 3; m/z: 350 (49, M^+), 307 (11), 306 (39), 184 (10), 172 (12), 123 (18), 117 (20, 113 (20), 109 (35), 107 (28), 101 (73), 100 (36), 99 (35), 97 (16), 93 (43), 89 (22), 87 (24), 85 (26), 83 (39), 81 (31), 79 (28), 76 (32), 75 (35), 73 (31), 72 (24), 71 (69), 59 (61), 57 (94), 45 (100), 43 (87). Exact mass. Calcd for $C_{19}H_{26}O_6$: 350.173. Found: 350.173.

Benzyl 4,6-cyclohexylidene-α-D-glucopyranoside (17). To a solution of dry benzyl α-D-glucopyranoside (16) (2.20 g, 8.14 mM), 1-ethoxycyclohexene (2.05 g, 16.28 mM) and anhydrous calcium sulfate (3 g) in anhydrous DMF (35 mL) at 4 °C was added p-toluenesulfonic acid (17 mg). The reaction mixture was kept at 4 °C with the exclusion of moisture for 48 h. Anhydrous sodium hydrogencarbonate (5 g) was added and the reaction mixture was stirred for 1 h at 0 °C. After chloroform (100 mL) was added, the mixture was kept at 5 °C for 12h, filtered and the filtrate concentrated to a yellowish syrup (2.36 g, 83%). Purification on a column of silica

gel (70 g), using solvent d as eluent, gave the title compound (17), a syrup (1.787 g, 63%); $[\alpha]_D^{25}$ +82.3° (c 1.07, chloroform; ^{1}H NMR δ 1.25 - 1.70 (complex m, 10 H, cyclohexylidene), 3.90 (br s, 1 H, exchanged with D_2O, OH), 4.49 (d, 1 H, J=11.82 Hz, benzylic H), 4.71 (d, 1 H, benzylic H), 7.32 (complex m, 5 H, phenyl); for remainder, see Tables 1 and 4; ^{13}C NMR δ 33.6, 29.7, 23.0, 23.0, 25.5 (cyclohexyl C), 100.5 (acetal C), 128.1, 128.2, 137.0 (Ph C), for remainder, see Table 3; m/z 350 (30, M^+), 307 (13, M-$^{\cdot}C_3H_7$), 259 (2, M-$^{\cdot}CH_2Ph$), 242 (2), 199 (10), 143 (10), 127 (9), 99 (21, $C_6H_{10}O^+H$), 98 (10), 97 (10), 92 (23), 91 (100, $^+CH_2Ph$), 81 (12), 69 (20), 55 (29), 43 (20), 42 (11), 41 (18). Exact mass. Calcd for $C_{19}H_{26}O_6$: 350.173. Found: 350.173.

Wittig Rearrangement of 17. To a stirred solution of 17 (0.680 g, 1.94 mM), and TMEDA (8.73 mM, 1.012 g) in dry THF (15 mL) under argon was slowly added a solution of n-butyllithium (8.73 mM, 4.85 mL, 2.0 M). The reaction mixture was refluxed for 20 h. Workup as previously gave a red syrup which was fractionated by column chromatography on silica gel (24 g), using solvent j as eluent into three fractions, A (0.175 g, 25%, R_f 0.47 in solvent j), B (0.103 g, 17%, R_f 0.47 and 0.34), and C (0.057 g, 8%, R_f 0.34). Fractions A and B were combined and refractionated on a column of silica gel (10 g) using solvent k as eluent to give three fractions, starting material (0.042 g, 6%), D (0.143 g, 21%), and E (0.054 g, 8%) (R_f 0.60, 0.45, 0.34 in solvent k).

Fraction D, a syrup, was 2,6-anhydro-5,7-O-cyclohexylidene-1-phenyl-D-erythro-L-gulo-heptitol (18), $[\alpha]_D^{26}$ +42.1° (c 2.54, chloroform); ^{1}H NMR δ 1.78 (br s, 2 H, exchanged with D_2O, OH), 1.96 (br s, 1 H, exchanged with D_2O, OH), 1.35 - 1.65 (complex m, 10 H, cyclohexyl), 7.33 (complex m, 5 H, phenyl), for remainder , see Tables 1 and 4; ^{13}C NMR δ 37.8, 27.7, 22.5, 22.7, 25.5 (cyclohexyl C), 99.9 (acetal C), 128.3, 128.5, 126.8, 140.1 (Ph C), for remainder, see Table 3; m/z 350 (10, M^+), 332 (2, M-H_2O), 307 (12, M-$^{\cdot}C_3H_7$), 245 (8), 244 (27), 226 (63), 225 (18), 201 (55), 198 (13), 184 (14), 183 (12), 171 (11), 149 (11), 141 (16), 131

(12), 129 (24), 128 (14), 127 (13), 123 (10), 121 (10), 117 (10), 115 (24), 114 (18), 113 (13), 107 (35), 105 (37, $^{+}$COPh), 99 (77, $C_6H_{10}O^{+}H$), 98 (53, $C_6H^{10}O^{+}$), 97 (42), 95 (19), 91 (48), 85 (34), 83 (29), 81 (48), 79 (31), 77 (34), 73 (36), 71 (40), 70 (36), 69 (82), 68 (18), 67 (16), 60 (11), 57 (51), 55 (100), 43 (88), 42 (36), 41 (82). Exact mass. Calcd for $C_{19}H_{26}O_6$: 350.173. Found: 350.174.

Fractions C and E (R_f 0.34 in solvent k) were 2,6-anhydro-5,7-O-cyclohexylidene-1-phenyl-D-erythro-L-ido-heptitol (19), $[\alpha]_D^{26}$ +40.3° (c 1.29, chloroform); ^{1}H NMR δ 1.35 - 1.70 (complex m, 10 H, cyclohexyl), 3.15, 3.65, 3.90 (3 br s, 3 H,, exchanged with D_2O, 3OH), 7.33 (complex m, 5 H, phenyl), for remainder, see Tables 1 and 4; ^{13}C NMRδ 37.8, 27.7, 22.5, 22.8, 25.5 (cyclohexyl C), 99.9 (acetal C), 126.4, 127.4, 128.2, 141.3 (Ph C), for remainder, see Table 3; m/z: 350 (10, M^{+}), 307 (9), 244 (6), 227 (44), 226 (100), 198 (13), 111 (43), 107 (26), 105 (21), 100 (23), 99 (70), 98 (55), 97 (34), 91 (35), 81 (36), 79 (25), 69 (61), 55 (79), 43 (49). Exact mass. Calcd for $C_{19}H_{26}O_6$: 350.173. Found: 350.174.

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