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**REGIOSELECTIVE BENZYLATION OF
PENTITOLS, TETRITOLS, AND SOME HEXITOLS
VIA THEIR STANNYL ETHER DERIVATIVES:
VERSATILE SYNTHESIS OF
MONOBENZYLALDITOLS**

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ABSTRACT

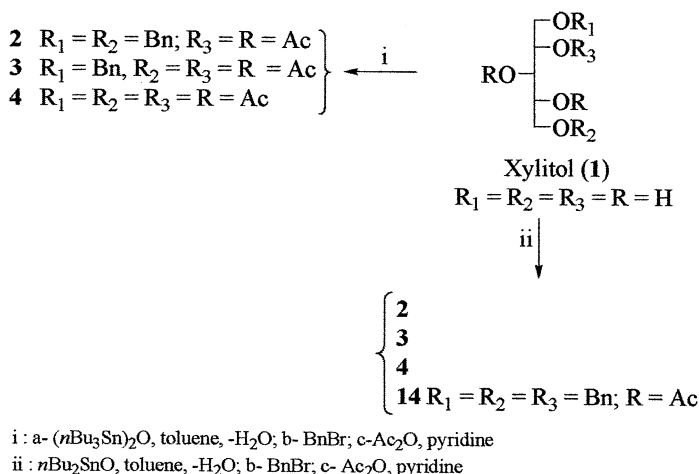
The xylitol, ribitol and D-arabinitol were transformed into their tributylstannyl ether derivatives by reaction with *bis*-tributyltin oxide [(*n*Bu₃Sn)₂O **I**] and azeotropic removal of water. Subsequent benzyl etherification, using BnBr with solvent or under free solvent conditions, led regioselectively to primary mono-*O*-benzylalditol derivatives in satisfactory yields for a direct regioselective synthesis (~ 52%). This etherification when applied to tetrیتols and some hexitols exhibits similar behaviour. With pentitols, an analogous study carried out with the *n*-dibutyltin oxide [*n*Bu₂SnO (**II**)] as the activating reagent showed contrasting results as regards regioselectivity.

INTRODUCTION

The regioselective etherification and esterification of unprotected polyols is a useful transformation in organic synthesis.^{1,2} A range of conditions for the regioselective introduction of a benzyl moiety has been described in the literature.^{3–5}

With alditols which contain more than three hydroxyl groups, the direct regioselective etherification of the primary alcohol functions are drastically limited,

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Scheme 1.

due to random etherification also occurring at the secondary hydroxyl groups. To avoid this difficulty with xylitol, a prior acetal protection step enables one free primary hydroxyl group to be conserved,⁶ and this can subsequently be esterified, etherified or thioetherified.⁷

More recently, efficient direct regioselective monoalkylation of symmetric 1,*n*-alkanediols (*n* = 2 to 10) *via* their dibutylstannylene acetal derivatives (using

Table 1. Benzoylation of Pentitols via Their

Entry	Substrate	Tin-reagent	Conditions			
			BnBr (eq.)	Tin-reagent (eq.)	Salt(eq)	Solvent
1	Xylitol (1)	(<i>n</i> -Bu ₃ Sn) ₂ O (I)	(2.5)	(4)	-	CCl ₄
2	"	"	"	"	-	without
3	"	"	"	"	-	"
4	Ribitol (5)	"	"	"	-	"
5	D-Arabinitol (9)	"	"	"	-	CCl ₄
6	Xylitol (1)	<i>n</i> -Bu ₂ SnO (II)	(1)	(2.5)	-	"
7	"	"	"	"	CsF(2)	"
8	"	"	(2.5)	"	-	"
9	"	"	(1)	"	NBu ₄ Br (2)	"
10	Ribitol (5)	"	"	"	-	"
11	"	"	(2.5)	(4)	-	"
12	"	"	"	"	-	"
13	D-Arabinitol (9)	"	(2)	(2.5)	-	"
14	"	"	(2.5)	(4)	-	"

PP = primary-primary; PS = primary-secondary; *With complex mixture; **peracetylated alditols



$n\text{Bu}_2\text{SnO}$ (**II**) as the activating reagent) has been reported.^{8a} For example, ribose diethyl dithioacetal has been converted into its 5-*O*-alkyl ether in good yield (68%) *via* the dibutylstannylene acetal.^{8b}

We have required some monobenzylated pentitols for use in recent thia and aza heterocyclic synthesis,⁹ the stannylene acetal complexes of pentitols being used as intermediates. Unfortunately, the only targeted primary monobenzyl derivative obtained was from xylitol.¹⁰

Herein, we report the regioselective primary mono benzylation of the pentitols, xylitol, ribitol and *D*-arabinitol, *via* their stannyl ether complexes (using $(\text{Bu}_3\text{Sn})_2\text{O}$ (**I**) as activating reagent). Next, this reaction was applied to tetritols, erythritol and *D,L*-threitol, and some hexitols, *D*-mannitol with C_2 -symmetry, *D*-glucitol and galactitol. The alditol stannyl ether derivatives were prepared by refluxing a mixture of bis-(tributyltin) oxide and alditols in toluene with azeotropic removal of the water formed.³

RESULTS AND DISCUSSION

The first regioselective pentitol *O*-benzylation attempt was carried out with xylitol (**1**) (Scheme 1) and $(n\text{Bu}_3\text{Sn})_2\text{O}$ (**I**) under the conditions reported in the Table 1 (entry 1). The expected 2,3,4,5-tetra-*O*-acetyl-1-*O*-benzyl-DL-xylitol (**3**) was obtained as the main product (45% yield) after acetylation and chromatogra-

Stannyl Ether or Stannylene Acetal Derivatives

T(°C)	Time(h)	Isolated yields (%)						Substrate (%)**
		Mono-(%)	di-(%)	tri-(%)				
reflux	120	3 (45)	2^{PP} (3)	-	-	4 (50)		
80	10	“ (50)	“ (10)	-	-	“ (30)		
90	20	“ (20)	“ (52)	-	-	“ (5)		
80	“	7 (52)	6^{PP} (16)	-	-	8 (23)		
reflux	65	11/12 (50)	10^{PP} (4)	-	-	13 (36)		
“	“	3 (60)	2^{PP} (5)	“	-	4 (33)		
rt	5	“ (53)	“ (23)	14^{1,2,5} (8)	“	“ (9)		
reflux	65	“ (28)	“ (52)	“	(17)	“ (0)		
rt	10	“ (10)	“	-	“	“ (85)		
65	65	7 (17)	6^{PP} (10)	mixture		8 (47)		
“	“	“ (26)	15^{ps (1,4)} (11)	(20)		“ (15)		
“	“	“ (31)	6^{PP} (8)	(17)		“ (32)		
50	40	“ (31)	6^{PP} (8)	(17)		“ (32)		
65	65	11/12 (25)	10^{PP} (4)	(13)		16^(1:4:5) (3)	13 (51)	
“	“	“ (20)	17^{p,s;(4:5)} (0)	(25)		“ (33)	13 (13)	
“	“	“ (20)	10^{PP} (0)	(25)		“ (33)	13 (13)	
“	“	“ (20)	17^{p,s;(4:5)} (0)	(25)		“ (33)	13 (13)	

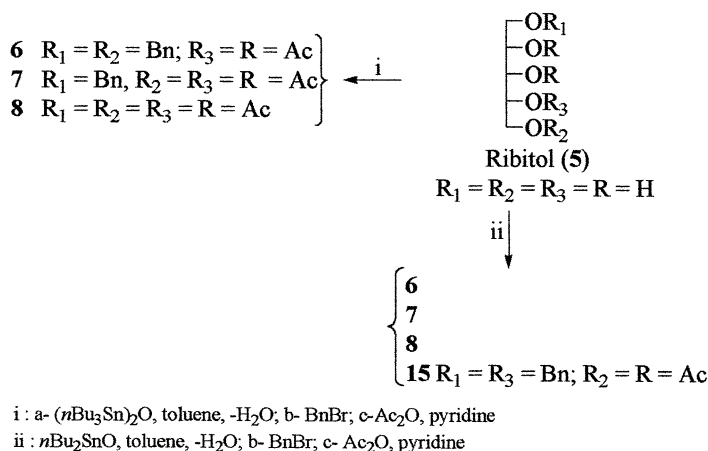


phy on silica gel. The 1,5-di-*O*-benzylxylitol derivative **2** was isolated in only a small amount (3%). The yield of monobenzylated derivative **3** reached 50% in a short time using solvent free conditions (entry 2). Increasing both reaction temperature (90 °C) and time (20 h) led to the 1,5-di-*O*-benzyl derivative **2** in good yield (52%, entry 3).

With the solvent free conditions reported in entry 4, ribitol (**5**) and the organotin reagent **I** gave the mono-*O*-benzylated and di-*O*-benzylated derivatives **7** and **6** in yields of 52 and 16%, respectively (Scheme 2). The monobenzylation of ribitol was slower than that of xylitol (entry 2), as 20 h were needed to complete the reaction. On the other hand, the attempt to favour the dibenzylated derivative **6** at a higher temperature and a long time (90 °C, 20 h) led to a complex mixture.

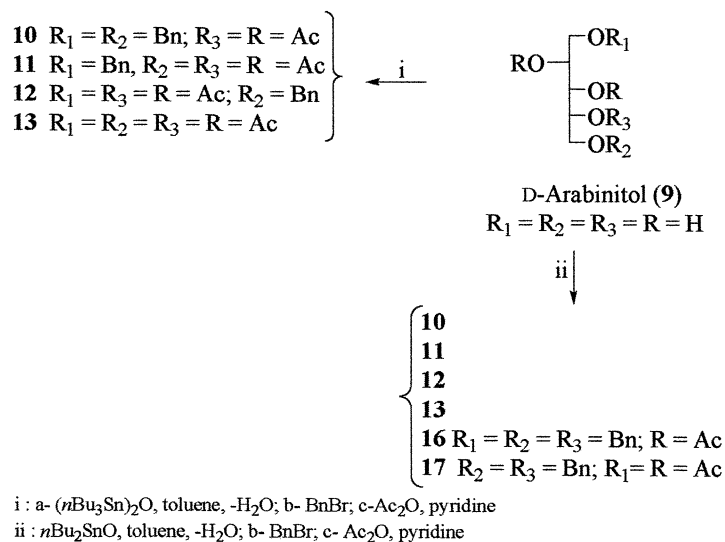
The stannyl ether complex of D-arabinitol (**9**) was submitted to both solvent-free conditions and using solvent. The solvent-free conditions appear to be drastic since compound **9** led mainly to a mixture of unidentified benzylated by-products. However, with chloroform as solvent, the D-arabinitol tin complex refluxed with BnBr for 65 h (entry 5) led, after acetylation (Scheme 3), to an equimolar mixture of regioisomeric 1-*O*-benzyl and 5-*O*-benzyl-D-arabinitol (or 1-*O*-benzyl-D-lyxitol) derivatives **11** and **12** in 50% overall yield (ratio determined by ¹³C NMR spectroscopy). The further *O*-benzylation of the second terminal primary alcohol group in the corresponding monoprotected tin complexes is slower. Only a 20% yield of the 2,3,4-tri-*O*-acetyl-1,5-di-*O*-benzyl-D-arabinitol (**10**) was obtained after 5 days in refluxing HCCl₃.

Compared with previous results obtained with the stannylene acetal intermediate (obtained with organotin oxide **II** as the activating reagent), xylitol appears to follow the same behaviour. Both the primary-primary di-*O*-benzylated and the primary mono-*O*-benzylated derivatives **2** and **3** were obtained mainly under conditions shown in entries 6 to 8, respectively.¹⁰ The use of only 1 equivalent of *n*Bu₂SnO favoured a selective formation of targeted mono-*O*-benzyl xylitol **3** in



Scheme 2.





Scheme 3.

good yield (60%, entry 6); the benzylation of secondary hydroxyl groups was excluded. Furthermore, under the same conditions, but in the presence of added cesium fluoride (2 equiv, entry 7), the benzylation occurred much faster (5 h instead of 65 h for complete reaction) without heating and with approximately the same regiochemistry. This salt effect was previously reported by Naguashima et al.¹¹ Surprisingly, tetrabutylammonium bromide (entry 9), which was conveniently used under nonpolar conditions, led to an unexpected decrease in reaction rate, and to a complex mixture when DMF was used as the aprotic polar solvent. Finally, the complete benzylation of both primary positions seems to depend on the organotin/substrate ratio used. Thus, 2.5 equiv of **II** (entry 8) instead of 1 equiv led to 1,5-di-*O*-benzylated derivative in 52% yield.

It should be emphasized, that use of added salt or base to the xylitol stannyl ether and benzyl bromide led to complex mixtures.

In comparison to xylitol, ribitol and D-arabinitol *O*-benzylation *via* the stannylene acetal (obtained with organotin reagent **II**) led, in addition to normally formed primary *O*-benzylated derivatives (**6**, **7**, **10**, **11** and **12**), to some unexpected primary-secondary di-*O*-benzylated by-products (**15**, **16** and **17**). The amount of secondary *O*-benzyl substitution seems to depend on the pentitol substrate; under moderate conditions, unsymmetrical D-arabinitol (**9**) gave, after acetylation of the crude product, a regioisomeric mixture of primary mono-*O*-benzyl derivatives **11** and **12** in 25% overall yield (one of them is in twofold majority) plus 1,2,3-tri-*O*-acetyl-4,5-di-*O*-benzyl-D-arabinitol (**17**) in a yield of 13% (entry 13). Only traces of primary di-*O*-benzyl derivative **10** (4%) and 1,4,5-tri-*O*-benzyl derivative **16** (3%) were isolated. With a large excess of BnBr (4 equiv, entry 14) the obtained yields of 4,5-di-*O*-benzylated and 1,4,5-tri-*O*-benzylated derivatives **17** and **16** were, respectively, 25 and 33%. Only a small amount of substrate remained (13%).



This result suggests that D-arabinitol was first transformed primarily into a mixture of regioisomeric mono-*O*-benzyl derivatives, 5-*O*-benzyl-D-arabinitol as major product and 1-*O*-benzyl-D-arabinitol as minor product, the former then undergoing regioselective *O*-benzylation of the secondary hydroxyl group at C-4. Further etherification took place subsequently at the primary C-1 alcohol.

It is of interest to note that a different regioselectivity behaviour was adopted by the stannylene acetal complex of ribitol (obtained with organotin complex **II**). While the vicinal 4,5-di-*O*-benzyl derivative **17** was formed from D-arabinitol, under the same conditions ribitol stannylene acetal as intermediate led to primary-secondary 1,4-di-*O*-benzyl derivative **15** (entry 11 to 13). No tri-*O*-benzylated derivative was detected.

In compound **17**, the secondary and the primary benzyl groups at C-4 and C-5 positions, respectively, were located by NMR spectroscopy (Table 2, 3 and 4). The ¹H NMR spectrum showed a large coupling constant of 6.9 Hz for *anti*-3,4-methine and a weak coupling constant of 3.7 Hz for *syn*-2,3-methine. These values

Table 2. ¹H Chemical Shifts (δ) for Peracetylated Mono,

	H-1	H-1'	H-2	H-3	H-4	H-4'	H-5
2 (<i>xylo</i>)	3.49(dd)	3.55(dd)	5.22(dd)	5.57(t)	5.22 (dd)		3.49 (dd)
3 "	2.40(dd)	2.36(dd)	5.13(m)	5.44(dd)	5.22(m)		4.24(dd)
4 "	3.80(dd)	4.13(dd)	5.10(dd)	5.20(t)	5.10(dd)		3.80(dd)
6 (<i>ribo</i>)	3.52(dd)	3.62(dd)	5.27(dd)	5.38(t)	5.27(dd)		3.52(dd)
7 "	3.48(dd)	3.58(dd)	5.25(m)	5.33(dd)	5.20(m)		4.09(dd)
8 "	4.40(dd)	4.63(dd)	5.66(dd)	5.80(t)	5.66(dd)		4.40(dd)
10 (<i>arabino</i>)	3.53(dd)	3.55(dd)	5.46(m)	5.43(dd)	5.16(m)		3.48(dd)
13 "	4.29(dd)	4.59(dd)	5.77(m)	5.88(dd)	5.57(m)		4.41(dd)
14 (<i>xylo</i>)	3.61(d)	3.61(d)	3.77(m)	5.50(dd)	5.34(m)		3.38(dd)
15 (<i>ribo</i>)	3.55(dd)	3.62(dd)	5.40(m)	5.40(m)	5.20(m)		4.10(dd)
16 (<i>arabino</i>)	3.55(dd)	3.59(dd)	5.48(m)	5.43(dd)	3.73(m)		3.59(dd)
17 "	4.00(dd)	4.23(dd)	5.50(m)	5.34(dd)	3.70(m)		3.50(dd)
19 (<i>threo</i>)	3.42(dd)	3.44(dd)	5.13(m)	5.28(m)	3.92(dd)	4.21(dd)	
20 "	3.55(m)	3.55(m)	5.14(m)	3.83(m)	4.02(dd)	4.15(dd)	
21 "	3.70(m)	3.70(m)	5.40(m)	4.00(m)	3.7(m)	3.70(m)	
25 (<i>erythro</i>)	3.50(dd)	3.55(dd)	5.18(m)	5.25(m)	4.15(dd)	4.27(dd)	
26 "	3.51(dd)	3.56(dd)	5.24(m)	3.70(m)	4.18(dd)	4.30(dd)	
27 "	3.68(dd)	3.75(dd)	5.42(m)	3.99(m)	3.80(dd)	3.83(dd)	
31 (<i>manno</i>)	3.43(dd)	3.52(dd)	5.07(m)	5.46(d)	5.46(d)		5.07(m)
32 "	3.43(dd)	3.52(dd)	5.05(m)	5.46(s)	5.41(s)		5.03(m)
35	3.41(dd)	3.45(dd)	5.06(m)	5.41(dd)	5.59(dd)		5.19(m)
38	4.36(dd)	4.55(dd)	5.50(m)	5.88(d)	5.88(d)		5.50(dd)
40 (<i>galacto</i>)	3.38(d)	3.38(d)	5.17(t)	5.33(s)	5.33(s)		5.17(t)
41	3.38(d)	3.38(d)	5.21(m)	5.35(dd)	5.30(dd)		5.19(m)



are consistent with the planar zig-zag conformation previously proposed for peracetylated¹² and 1,5-dihalogenated D-arabinitol derivatives.¹³ Subsequently, the vicinal 4,5-di-*O*-benzyl positions were indicated by ¹³C NMR shift correlation. The same study was carried out for the tribenzylated and dibenzylated derivatives **16** and **10**; these produced the same $J_{3,4}$ - $J_{2,3}$ *anti-syn* methine sequence.

The synthesis in satisfactory yields of primary monobenzylated pentitols *via* their stannyl ether derivatives, allowed us to expand this reaction to tetritols and some hexitols (Tables 5 and 6). Thus, we showed that with tetritol stannyl ether complexes, the monobenzylation occurred in good yields using solvent-free conditions. Furthermore, we observed that the rate of primary regioselective *O*-benzylation of D,L-threitol (**18**) was faster than of erythritol (**24**). In fact, while only 5 h were needed to obtain the 1-*O*-benzyl-D,L-threitol derivative **19** in 54% yield (entry 1, Table 6), 20 h were required to obtain 1-*O*-benzyl-D,L-erythritol derivative **25** in 50% yield (entry 3). On the other hand, in both cases, 1,3-di-*O*-benzylated derivatives were isolated as by-product in minor yields. With erythritol, the yield

 Di, and Tri-*O*-benzylated Alditol Derivatives (in CDCl₃)

H-5'	H-6	H-6'	CH ₃	CH ₂ (Bn)	Ph(Bn)
3.55 (dd)			2.02(s) (6H); 1.99(s, 3H)	4.45(s)(4H)	7.29(m)(10H)
3.92(dd)			2; 1.98; 1.93		
4.13(dd)			1.84(s, 6H); 1.89(s, 3H)		
3.62(dd)			1.92(s, 6H); 1.99(s, 3H)	4.46(s, 4H)	7.29(m, 10H)
4.29(dd)			2.03; 1.98; 1.95	4.44(s, 2H)	7.24 (m, 5H)
4.63(dd)			2(s, 6H); 2.1(s,9H)	-	-
3.60(dd)			2.05; 1.98; 1.92	4.45(m,4H)	7.20(m, 10H)
4.54(dd)			2.07(m, 12H)		
3.49(dd)			2.10(s, 6H)	4.49(s, 6H)	7.30(m, 15H)
4.30(dd)			2.02; 2; 1.96	4.38(s, 4H)	7.24(m, 5H)
3.61(dd)			2; 1.96	4.48(m, 6H)	7.27(m, 15H)
3.62(dd)			2.01; 1.98; 1.91	4.55(m, 4H)	7.26(m, 10H)
			1.89; 1.91; 1.95	4.36(dd, 2H)	7.19(m, 5H)
			1.29; 1.98	4.47(d); 4.40(d)	7.25(m, 10H)
			2.08	4.81(dd); 4.68(dd)	7.3(m)
			1.94; 1.96; 2.00	4.45(dd)	7.24(m)
			1.98(s, 6H)	4.50(dd); 4.12(dd)	7.25(m)
			2.07	4.74(dd); 4.78(dd)	7.39(m)
	3.43(dd)	3.52(dd)	2.10(m, 12H)	4.47(d); 4.40(d)	7.24(m)
	4.01(dd)	4.17(dd)	2.03(m, 15H)	4.47(dd)	7.25(m)
	3.58(dd)	3.62(dd)	1.98(m, 12H)	4.43(m, 4H)	7.23(m)
	4.36(dd)	4.55(dd)	2.13; 2.11; 2.03		
	3.38(d)	3.38(d)	2.01; 1.96	4.34(dd); 4.42(dd)	7.23(m)
	3.77(dd)	4.20(dd)	2.01; 1.94	4.34(dd); 4.42(dd)	7.24(m)



Table 3. Coupling Constants (Hz) for Peracetylated Mono, Di, and Tri-*O*-benzylated Alditol Derivatives (in CDCl₃)

Compd.	Coupling constants (Hz)												
	$J_{1,1'}$	$J_{1,2}$	$J_{1',2}$	$J_{2,3}$	$J_{3,4}$	$J_{3,4'}$	$J_{4,4'}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
2(xylo)	10.6	4.6	5.2	5.4	5.4			4.6	5.2	10.6			
3 "	10.7	4.8	4.7	5.4	5.4			4.6	6.2	11.9			
4 "	12	6.2	4.3	5.3	5.3			6.2	4.3	12			
6(ribo)	12.6	6.2	3.7	5.4	5.4			6.2	3.7	12.6			
7 "	10.7	5.8	4.0	5.2	5.2			6.4	3.0	12.2			
8 "	12.3	3.3	6.1	5.7	5.7			3.3	6.1	12.3			
10(arabino)	10.3	7.3	3.8	3.1	7.9			7.4	5.7	10.8			
13 "	11.9	6.9	4.6	2.3	8.6			5.1	2.6	12.4			
14(xylo)	-	5.0	5.0	6.2	4.4			5.2	4.0	10.8			
15(ribo)	10.5	5.7	3.2	-	-			5.3	3.4	12.2			
16(arabino)	10.7	7.5	3.5	4.4	5.8			6.0	4.2	10.3			
17 "	11.8	6.3	5.0	3.7	6.9			5.0	4.2	10.3			
19(threo)	-	4.0	4.0	0.0	5.3	3.1	12.1						
20 "	10.5	5.9	3.9	0.0	6.1	4.5	11.6						
21 "	10.2	5.7	-	4.4	-	5.0	10.4						
25(erythro)	10.7	5.4	4.3	5.8	6.2	3	12.5						
26 "	10.8	5.5	4.3	5.6	6.6	2.7	12.7						
27 "	10.7	5.4	4.3	5.8	5.7	4.2	11.0						
31(manno)	10.8	5.4	3.9	8.3	-			8.3		5.4	3.9	10.8	
32 "	10.7	5.1	3.8	9.3	2.0			8.8		5.2	2.5	12.5	
35(glu)	8.6	5.6	3.1	4.2	6.1			4.5		5.2	2.5	12.5	
38 "	12.4	5.1	2.8	5.9	-			5.9		5.1	2.8	12.4	
40(galacto)	-	6	6	0	-			0		6	6	-	
41 "	-	5	5	9.9	-			10.5		8.1	4.2	11.1	

of 1,3 primary-secondary di-*O*-benzyl derivative **26** reached 50% using a large excess of BnBr (entry 4). Furthermore, with both D,L-threitol and erythritol, simultaneous use of a large excess of BnBr and a long reaction time (20 h) led mainly to the tribenzylated derivatives **21** (62%, entry 2) and **27** (60%, entry 5), respectively.

Finally the more complex hexitols namely, D-mannitol (**30**), D-glucitol (**34**) and galactitol (**39**), transformed to their stannyl ether derivatives, led after benzylation, to the corresponding monobenzyl ethers **32**, **36/37** and **41** in reasonable yields (45 to 48%) (entries 6 to 9, Table 6).

In conclusion, from a synthetic point of view, the most interesting result to note in this work is the generalized regioselective benzylation (*via* the tributylstannyl ether complex) at only one primary position of alditols, and often under



solvent-free conditions. The monobenzylated derivatives were obtained in satisfactory yields for a direct regioselective synthesis (47 to 54%). Current work is directed towards studying the reactivity of alditols organotin complexes towards other electrophiles.

EXPERIMENTAL

General methods. Melting points were determined with a Buchi 535 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on Bruker 300 WB spectrometer; chemical shifts are reported in δ (ppm) relative to Me_4Si . Coupling constants, assigned by double irradiation, are in Hz. All ^{13}C NMR signals were assigned through C,H-correlated spectra. TLC was performed on silica Gel 60 F₂₅₄ 230 mesh (E. Merck) with hexane-EtOAc as eluent, and zones were detected by vanillin- H_2SO_4 reagent. The silica gel used in column chromatography was 35–70 m (Amicon). Mass spectroscopy analyses were performed by the “Service d’Analyse de la Faculté de Pharmacie, Laboratoire de Chimie Thérapeutique U.R.A. au CNRS, (Université de Reims Champagne Ardenne)”. Elemental analyses were performed by the “Service de Microanalyse du CNRS” (Laboratoire de Bioorganique, Université de Reims Champagne Ardenne”.

General procedure for *O*-benzylation via the stannyl ether complex. The alditol (0.2 g) was allowed to react with the $(n\text{Bu}_3\text{Sn})_2\text{O}$ (**I**) in refluxing toluene (20 mL). After azeotropic removal of water over 5 h the solvent was evaporated under vacuum. The syrup obtained was dried and submitted to *O*-benzylation under conditions reported in Tables 1 and 2. The crude product was dried and peracetylated with excess of acetic anhydride in pyridine at room temperature. After extraction following the usual procedure, the syrup obtained was treated with aqueous KF^{14} (20%) overnight. The organotin residue was filtered and the crude product was chromatographed on silica gel with a mixture of hexane-ethyl acetate as eluent. From the alditols studied, the following products were isolated in the reported yields under optimal conditions of monobenzylated derivatives (see Tables 1 and 2).

From xylitol (**1**) (for conditions see entry 2, Table 1):

2,3,4-Tri-*O*-acetyl-1,5-di-*O*-benzylxylitol (2). Syrup; Yield 60 mg (10%); R_f 0.49 in 5:2 hexane-EtOAc; MS: m/z 459, M ($\text{C}_{25}\text{H}_{30}\text{O}_8$) 458.50; Anal. Calcd for $\text{C}_{25}\text{H}_{30}\text{O}_8$: C, 65.49; H, 6.60; O, 27.92. Found: C, 65.77; H, 6.68.

2,3,4,5-Tetra-*O*-acetyl-1-*O*-benzyl-D,L-xylitol (3). Syrup; Yield 270 mg (50%); R_f 0.37 in 5:2 hexane-EtOAc; MS: m/z 411 [M + 1], M ($\text{C}_{20}\text{H}_{26}\text{O}_9$) 410.42. Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_9$: C, 58.53; H, 6.39; O, 35.09. Found: C, 58.90; H, 6.42.

The di-*O*-benzyl derivative **2** was obtained in major part (50%) in conditions reported in entry 4.



Table 4. ^{13}C Chemical Shifts (δ) for Peracetylated Mono,

<i>Compd</i>	C-1	C-2	C-3	C-4	C-5	C-6	CO(Ac)
2	68.1	70.5	69.9	70.5	68.1		169.4; 170.1
3	67.7	69.3	70.3	69.3	61.8		169.6; 169.8; 170; 170.2
4	60.9	68.2	68.2	68.2	60.9		168.5; 168.7; 169
6	67.9	69.4	70.2	69.4	67.9		169.4; 169.9; 170.6
7	67.7	69.7	70.3	69.7	61.9		169.3; 169.7; 169.8; 170.5
8	61.8	69.8	69.3	69.8	61.8		169.8; 169.5; 170.2
10	68.3	69.0	70.3	69.3	61.8		169.6; 169.8; 170; 170.2
11/ 12	67.90, 67.72, 62.02 or 61.62	68.71	68.18	68.71	67.90, 67.72, 62.02 or 61.62		169.51; 169.77; 170.34
13	62.9	68.2	69.4	68.7	62.5		170.4; 170.6; 170.7
14	69.7	76.2	71.2	71.1	68.2		170.1
15	66.9	70.7	71.8	73.9	61.2		169.5; 168.7; 168.3
16	64.4	70.2	70.5	76.0	68.7		169.9; 170.1
17	62.7	69.2	70.0	75.6	69.0		169.7; 169.9; 170.3
19	67.6	70.0	69.4	61.9			169.85; 169.74
20	67.68	71.49	77.46	62.87			170.29; 170.62
21	68.72	71.26	75.85	67.36			169.48
25	60.97	68.81	69.19	66.63			168.88; 169.59
26	62.67	75.18	71.18	67.86			169.04
27	68.42	76.91	72.08	69.75			169.5
29	68.39	68.32	68.56	68.56	68.32	68.39	169.68; 169.93
31	62.7	68.5	68.9	68.9	68.5	62.7	170.9; 170.4
32	68.21	68.49	68.04	67.56	67.84	61.84	169.65; 169.92; 170.53
33	67.64	68.99	69.75	70.48	68.99	67.92	169.77; 170.23
36/37	67.21 or 67.72	-	-	-	-	60.49 or 60.77	169.20
40	68.3	68.4	67.9	67.9	68.4	68.3	169.37; 168.82
41	67.6	67.63	67.63	67.63	67.63	62.21	170.24; 169.74

* In mixture with **12**; ** In mixture with **11**



VERSATILE SYNTHESIS OF MONOBENZYLALDITOLS

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Di, and Tri-*O*-benzylated Alditol Derivatives (in CDCl₃)

Me(Ac)	CH ₂ (Bn)	Ph (Bn)	C-ipso
20.5; 20.7	73.2	128.3; 127.7	137.5
20.5; 20.6; 20.7	73.3	128.3; 127.7	137.4
19.3; 19.4; 19.5	-	-	-
20.9; 20.7	73.1	128.3; 128; 127.7	137.6
20.6; 20.7; 20.9	73.1	128	137.5
20.2; 20.4	-	-	-
20.5; 20.9; 20.7	73.3	128.3; 127.7	137.4
20.49	73.25	128.30; 127.73	137.32
20.8; 20.9; 21	-	-	-
20.9; 20.8	73.5; 73.1; 72.5	128.3; 127.9; 127.7	137.9; 137.7
19.7; 19.5	69.6; 69.0	127.1; 126.8	136.5; 136.2
20.9; 20.7	73.4; 73.2; 72.4	128.3; 128.1; 127.7	137.9
20.6	73.5; 72.5	128.3; 128.1; 127.8	137.7; 137.4
20.59; 20.51	73.1	127.62; 128.29	137.45
20.76; 20.94	73.21	127.65; 127.83; 127.95; 128.35	137.68
20.20	72.27; 72.42; 72.58	126.88; 127.11; 127.24; 127.56	137.18; 137.30; 137.58
19.67; 19.79 20.90	72.22	127.39; 126.71	137.53
21.13	73.13; 73.39; 73.43	128.2	137.3
20.60; 20.91	73.22	127.66; 127.78; 128.28	137.53
21.2; 20.9			
20.55; 20.77; 20.89	73.26	127.82; 128.29	137.43
20.77; 20.63	73.07; 73.29	127.8	137.61
20.58	73.20	127.27	136.37; 136.58
19.88; 19.66	72.35	127.36; 126.79	136.61
20.55	73.32	128.31; 127.73	137.48



Table 5. Summary of Benzylated Tetritol and Hexitol Derivatives Obtained via the Corresponding Stannyl Ether Complexes

Substrate	Isolated Products*
$\begin{array}{l} \text{HO} - \begin{cases} \text{OH} \\ \text{OH} \\ \text{OH} \end{cases} \\ \text{D,L-Threitol (18)} \end{array}$	$\begin{array}{l} \text{RO} - \begin{cases} \text{OR}_1 \\ \text{OR}_3 \\ \text{OR}_2 \end{cases} \\ \\ \\ \text{RO} - \begin{cases} \text{OR}_1 \\ \text{OR} \\ \text{OR}_3 \\ \text{OR}_2 \end{cases} \end{array}$ <p>19 R₁ = Bn; R = R₂ = R₃ = Ac 20 R₁ = R₃ = Bn; R = R₂ = Ac 21 R₁ = R₂ = R₃ = Bn; R = Ac 23 R₁ = R₂ = R₃ = R = Ac</p>
$\begin{array}{l} \begin{cases} \text{OH} \\ \text{OH} \\ \text{OH} \\ \text{OH} \end{cases} \\ \text{Erythritol (24)} \end{array}$	$\begin{array}{l} \text{RO} - \begin{cases} \text{OR}_1 \\ \text{OR} \\ \text{OR} \\ \text{OR}_2 \end{cases} \\ \\ \\ \text{RO} - \begin{cases} \text{OR}_1 \\ \text{OR} \\ \text{OR} \\ \text{OR}_2 \end{cases} \end{array}$ <p>25 R₁ = Bn; R = R₂ = R₃ = Ac 26 R₁ = R₃ = Bn; R = R₂ = Ac 27 R₁ = R₂ = R₃ = Bn; R = Ac 29 R₁ = R₂ = R₃ = R = Ac</p>
$\begin{array}{l} \text{RO} - \begin{cases} \text{OR}_1 \\ \text{OR} \\ \text{OR} \\ \text{OR}_2 \end{cases} \\ \text{D-Mannitol (30)} \end{array}$	$\begin{array}{l} \text{RO} - \begin{cases} \text{OR}_1 \\ \text{OR} \\ \text{OR} \\ \text{OR}_2 \end{cases} \\ \\ \\ \text{RO} - \begin{cases} \text{OR}_1 \\ \text{OR} \\ \text{OR} \\ \text{OR}_2 \end{cases} \end{array}$ <p>31 R₁ = R₂ = Bn; R = Ac 32 R₁ = Bn; R₂ = R = Ac 33 R₁ = R₂ = R = Ac</p>
$\begin{array}{l} \text{RO} - \begin{cases} \text{OR}_1 \\ \text{OR} \\ \text{OR} \\ \text{OR}_2 \end{cases} \\ \text{D-Glucitol (34)} \end{array}$	$\begin{array}{l} \text{RO} - \begin{cases} \text{OR}_1 \\ \text{OR} \\ \text{OR} \\ \text{OR}_2 \end{cases} \\ \\ \\ \text{RO} - \begin{cases} \text{OR}_1 \\ \text{OR} \\ \text{OR} \\ \text{OR}_2 \end{cases} \end{array}$ <p>35 R₁ = R₂ = Bn; R = Ac 36 R₁ = Bn; R₂ = R = Ac 37 R₁ = R = Ac; R = Bn 38 R₁ = R₂ = R = Ac</p>
$\begin{array}{l} \text{RO} - \begin{cases} \text{OR}_1 \\ \text{OR} \\ \text{OR} \\ \text{OR}_2 \end{cases} \\ \text{Galactitol (39)} \end{array}$	$\begin{array}{l} \text{RO} - \begin{cases} \text{OR}_1 \\ \text{OR} \\ \text{OR} \\ \text{OR}_2 \end{cases} \\ \\ \\ \text{RO} - \begin{cases} \text{OR}_1 \\ \text{OR} \\ \text{OR} \\ \text{OR}_2 \end{cases} \end{array}$ <p>40 R = R₂ = Bn; R = Ac 41 R₁ = Bn; R₂ = R = Ac 42 R₁ = R₂ = R = Ac</p>

* After acetylation of crude product

Table 6. Benzylation of Tetritols and Some

Entry	Substrate	Conditions					
		Tin-reagent	(eq)	BnBr (eq)	Solvent	T(°C)	Time(h)
1	D,L-Threitol (18)	(n-Bu ₃ Sn) ₂ O	(1)	(1.2)	without	80	5
2	"	"	(2.5)	(4)	"	"	20
3	Erythritol (24)	"	(1)	(1.2)	"	"	"
4	"	"	(2.5)	(4)	"	"	5
5	"	"	"	"	"	"	20
6	D-Mannitol (30)	"	"	"	HCCl ₃	"	240
7	"	"	"	"	without	"	20
8	D-Glucitol (34)	"	"	"	"	70	25
9	Galactitol (39)	"	(4)	"	"	"	30

PP = primary-primary; P^S = primary-secondary; *With complex mixture; **peracetylated alditols

From ribitol (**5**) (for conditions see entry 4, Table 1) :

2,3,4-Tri-*O*-acetyl-1,5-di-*O*-benzylribitol (6). Syrup; Yield 96 mg (16%); R_f 0.67 in 5:3 hexane-EtOAc; MS: m/z 459, M ($C_{25}H_{30}O_8$) 458.50.

Anal. Calcd for $C_{25}H_{30}O_8$: C, 65.49; H, 6.60; O, 27.92. Found: C, 65.56; H, 6.65.

2,3,4,5-Tetra-*O*-acetyl-1-*O*-benzyl-D,L-ribitol (7). Syrup; Yield 280 mg (52%); R_f 0.55 in 5:2 hexane-EtOAc; MS: m/z 411 [M + 1], M ($C_{20}H_{26}O_9$) 410.42.

Anal. Calcd for $C_{20}H_{26}O_9$: C, 58.53; H, 6.39; O, 35.09. Found: C, 58.72; H, 6.50.

From D-arabinitol (**9**) (for conditions see entry 5, Table 1) :

2,3,4-Tri-*O*-acetyl-1,5-di-*O*-benzyl-D-arabinitol (10). Syrup; Yield 24 mg (4%); R_f 0.67 in 5:3 hexane-EtOAc; MS: m/z 459, M ($C_{25}H_{30}O_8$) 458.50.

Anal. Calcd for $C_{25}H_{30}O_8$: C, 65.49; H, 6.60; O, 27.92. Found: C, 65.82; H, 6.63.

2,3,4,5-Tetra-*O*-acetyl-1-*O*-benzyl-D-arabinitol (11) and 1,2,3,4-tetra-*O*-acetyl-5-*O*-benzyl-D-arabinitol (12). Syrup; Yield 270 mg (50%); R_f 0.52 in 5:3 hexane-EtOAc; MS: m/z 411 [M + 1], M ($C_{20}H_{26}O_9$) 410.42.

Anal. Calcd $C_{20}H_{26}O_9$: C, 58.53; H, 6.39; O, 35.09. Found: C, 58.80; H, 6.52.

From D,L-threitol (**18**) (for conditions see entry 1, Table 6) :

2,3,4-Tri-*O*-acetyl-1-*O*-benzyl-D,L-threitol (19). Syrup Yield 299 mg (54%); R_f 0.38 in 6:2 hexane-EtOAc; MS: m/z 339 [M + 1], M ($C_{17}H_{22}O_7$) 338.35.

Anal. Calcd for $C_{17}H_{22}O_7$: C, 60.35; H, 6.55; O, 33.10. Found: C, 60.41; H, 6.63.

2,4-Di-*O*-acetyl-1,3-di-*O*-benzyl-D,L-threitol (20). Syrup; Yield 95 mg (15%); R_f 0.41 in 6:2 hexane-EtOAc; MS: m/z 387 [M + 1], M ($C_{22}H_{26}O_6$) 386.44.

Hexitols via Their Stannyl Ether Derivatives

<i>Isolated yields (%)</i>							
	Mono-(%)		di-(%)		tri-(%)		Substrate (%)**
19	(54)	20^{PS} (1:3)	(15)	21^{1,3,4}	(0)	23	(27)*
"	(0)	"	(17)	"	(62)	"	(0)*
25	(50)	26^{PS} (1:3)	(13)	27	(0)	29	(36)*
"	(30)	"	(50)	"	(10)	"	(3)*
"	(5)	"	(15)	"	(60)	"	(0)*
32	(45)	31^{PP}	(0)	-	-	33	(31)*
"	(36)	"	(5)	-	-	"	(49)*
36/37	(48)	35^{PP}	(23)	-	-	38	(29)
41	(47)	40^{PP}	(21)	-	-	42	(25)



Anal. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78; O, 24.84. Found: C, 68.75; H, 6.81.

From D,L-threitol (**18**) (for conditions see entry 2, Table 5) : The di-*O*-benzyl derivative **20** was obtained in 17% yield plus:

2-*O*-acetyl-1,3,4-tri-*O*-benzyl-D,L-threitol (21). Syrup; Yield 441 mg (62%); R_f 0.56 in 6:2 hexane-EtOAc; MS: m/z 435 [M + 1], M ($C_{27}H_{30}O_5$) 434.21.

From erythritol (**24**) (three sets of conditions):

Entry 3, Table 6: Optimal conditions for primary monobenzylated derivative:

2,3,4-Tri-*O*-acetyl-1-*O*-benzyl-D,L-erythritol (25). Syrup; Yield 277 mg (50%); R_f 0.30 in 6:2 hexane-EtOAc; MS: m/z 339 [M + 1], M ($C_{17}H_{22}O_7$) 338.35.

Anal. Calcd for $C_{17}H_{22}O_7$: C, 60.35; H, 6.55; O, 33.10. Found: C, 60.83; H, 6.57.

2,4-Di-*O*-acetyl-1,3-di-*O*-benzyl-D,L-erythritol (26). Syrup; Yield 82 mg (13%); Syrup; R_f 0.41 in 6:2 hexane-EtOAc; MS: m/z 387 [M + 1], M ($C_{22}H_{26}O_6$) 386.44.

Anal. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78; O, 24.84. Found: C, 68.88; H, 6.90.

Entry 4, Table 6: Optimal conditions for 1,3-dibenzylated derivative **26** (50%).

Entry 5, Table 6: Optimal conditions for 1,3,4-tribenzylated derivative **27**:

2-*O*-Acetyl-1,3,4-tri-*O*-benzyl-D,L-erythritol (27). Syrup; Yield 427 mg (60%); Syrup; R_f 0.58 in 6:2 hexane-EtOAc; MS: m/z 435 [M + 1], M ($C_{27}H_{30}O_5$) 434.21.

From D-mannitol (**30**) (for conditions see entry 6, Table 6):

2,3,4,5,6-Penta-*O*-acetyl-1-*O*-benzyl-D-mannitol (32). Syrup; Yield 238 mg (45%); R_f 0.44 in 5:3 hexane-EtOAc; MS: m/z 483 [M + 1], M ($C_{23}H_{30}O_{11}$) 482.48.

Anal. Calcd for $C_{23}H_{30}O_{11}$: C, 57.26; H, 6.27; O, 36.48. Found: C, 57.68; H, 6.35.

Under conditions reported in entry 7, the 1,6-dibenzylated derivative was obtained as minor product :

2,3,4,5-Tetra-*O*-acetyl-1,6-di-*O*-benzyl-D-mannitol (31). Syrup; Yield 29 mg (5%); R_f 0.52 in 5:3 hexane-EtOAc; MS: m/z 531 [M + 1], M ($C_{28}H_{34}O_{10}$) 530.56.

Anal. Calcd for $C_{28}H_{34}O_{10}$: C, 63.39; H, 6.46; O, 30.16. Found: C, 63.45; H, 6.49.

From D-glucitol (**34**) (for conditions see entry 8, Table 5) :

2,3,4,5,6-Penta-*O*-acetyl-1-*O*-benzyl-D-glucitol (36) and 1,2,3,4,5-penta-*O*-acetyl-6-*O*-benzyl-D-glucitol (37). Syrup; Yield 254 mg (48%); R_f 0.34 in 5:3 hexane-EtOAc; MS: m/z 483 [M + 1], M ($C_{23}H_{30}O_{11}$) 482.48.



Anal. Calcd for $C_{23}H_{30}O_{11}$: C, 57.26; H, 6.27; O, 36.48. Found: C, 57.73; H, 6.38.

2,3,4,5-Tetra-*O*-acetyl-1,6-di-*O*-benzyl-D-glucitol (35). Syrup; Yield 134 mg (23%); R_f 0.47 in 5:3 hexane-EtOAc; MS: m/z 531 [M + 1], M ($C_{28}H_{34}O_{10}$) 530.56.

Anal. Calcd for $C_{28}H_{34}O_{10}$: C, 63.39; H, 6.46; O, 30.16. Found: C, 63.72; H, 6.49.

From galactitol (**39**) (for conditions see entry 9, Table 5):

2,3,4,5-Tetra-*O*-acetyl-1,6-*O*-benzylgalactitol (40). Yield 122 mg (21%); mp 149–151 °C; R_f 0.55 in 5:3 hexane-EtOAc; MS: m/z 531 [M + 1], M ($C_{28}H_{34}O_{10}$) 530.56.

Anal. Calcd for $C_{28}H_{34}O_{10}$: C, 63.39; H, 6.46; O, 30.16. Found: C, 63.68; H, 6.52.

2,3,4,5,6-Penta-*O*-acetyl-1-*O*-benzyl-D,L-galactitol (41). Yield 249 mg (47%); mp 138 °C; R_f 0.39 in 5:3 hexane-EtOAc; MS: m/z 483 [M + 1], M ($C_{23}H_{30}O_{11}$) 482.48.

Anal. Calcd for $C_{23}H_{30}O_{11}$: C, 57.26; H, 6.27; O, 36.48. Found: C, 57.33; H, 6.27.

General procedure for benzyl etherification of pentitols via the stannylene acetal complex. A mixture of pentitols (0.2 g) and dibutyltin oxide in toluene was refluxed for 16 h with azeotropic removal of water. The white powder obtained after removal of the solvent was dried under vacuum and treated with benzyl bromide under the conditions reported in Table 1. The crude product obtained was subsequently acetylated (Ac_2O in pyridine overnight at room temperature). The syrup obtained after concentration of the solution was dissolved in ethyl ether and treated with 2,2'-bipyridyl to precipitate organotin compounds. The filtrate was concentrated to dryness to give a residue which was processed by column chromatography on silica gel using a mixture of hexane-AcOEt as eluant.

From xylitol (**1**): for optimal conditions in monobenzylated derivative **3** see entry 6, Table 1. The previously described mono and dibenzylated derivatives **3** and **2** were obtained, respectively, in 60 and 5% yields plus:

3,4-Di-*O*-acetyl-1,2,5-tri-*O*-benzyl-D,L-xylitol (14). Syrup; Yield 20 mg (3%); R_f 0.65 in 5:2 hexane-EtOAc.

Anal. Calcd for $C_{30}H_{34}O_7$: C, 71.15; H, 6.72; O, 22.13. Found: C, 71.02; H, 6.68.

For optimal conditions in dibenzylated derivative **2** see entry 8, Table 1. The previously described mono, di and tribenzylated derivatives **3**, **2** and **14** were obtained in 28, 52 and 17% yields respectively.

From ribitol (**5**): for conditions see entry 4, Table 1. The previously described mono and dibenzylated derivatives **7** and **6** were obtained, respectively, in 31 and



8% yields plus:

2,3,5-Tri-*O*-acetyl-1,4-di-*O*-benzyl-D,L-ribitol (15). Syrup; Yield 102 mg (17%); R_f 0.62 in 5:3 hexane-EtOAc; MS: m/z 459 [M + 1], M(C₂₅H₃₀O₈) 458.50.

Anal. Calcd for C₂₅H₃₀O₈: C, 65.49; H, 6.60; O, 27.92. Found: C, 65.67; H, 6.63.

From D-arabinitol (**9**): for conditions see entry 14, Table 1. The previously described monobenzylated derivatives **11** and **12** were obtained in 20% overall yields plus:

2,3-Di-*O*-acetyl-1,4,5-tri-*O*-benzyl-D-arabinitol (16). Syrup; Yield 220 mg (33%); R_f 0.60 in 5:2 hexane-EtOAc; MS: m/z 507 [M + 1] M(C₃₀H₂₄O₇) 506.6.

Anal. Calcd for C₃₀H₂₄O₇: C, 71.15; H, 6.72; O, 22.13. Found: C, 71.23; H, 6.75.

1,2,3-Tri-*O*-acetyl-4,5-di-*O*-benzyl-D-arabinitol (17). Syrup; Yield 151 mg (25%); Syrup; R_f 0.47 in 5:2 hexane-EtOAc; MS: m/z 459 [M + 1] M(C₂₅H₃₀O₈) 458.5.

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