Reductive Fragmentation of Carbohydrate Anomeric Alkoxy Radicals. Synthesis of Alditols with Potential Utility as Chiral Synthons

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A series of anomeric nitrate esters and *N*-phthalimido glycosides of carbohydrates in furanose and pyranose forms have been synthesized in order to generate the corresponding alkoxy radicals and study the C1−C2 fragmentation reaction under reductive conditions. This reaction constitutes a two-step method for the transformation of carbohydrates into the corresponding alditols with one less carbon. Using this methodology, interesting four- and five-carbon building blocks for natural products synthesis possessing D-erythritol, D-threitol, D-xylitol, and D-arabinitol stereochemistry have been prepared. The synthesis of 1,2-*O*-isopropylidene-*β*-L-threose (**40**) and 1-acetamido-2,4,5-tri-*O*-acetyl-D-arabinitol (**50**) have also been achieved from 1,2:5,6-di-*O*-isopropylidene-*β*-D-glucofuranose and 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranose, respectively.

The preparation of chiral synthons from carbohydrates has received considerable attention from organic chemists.[1] Among them, homochiral erythritol[2] and threitol[3] derivatives are important four-carbon building blocks for natural product synthesis. Two characteristics of these compounds are of special interest from the synthetic point of view: the related alcohols in the chiral threitols are homotopic groups due to the C_2 axis of symmetry,[3a,d,h] and *meso*-erythritol can be transformed into chiral derivatives by appropriate desymmetrization.[4,2c,e,h] This last feature is of interest when an enantiodivergent synthesis is planned since, in this case, the related alcohols are enantiotopic groups.

In previous papers from this laboratory, we have described the facile formation of glycopyran-1-*O*-yl and glycofuran-1-*O*-yl radicals by reaction of carbohydrate anomeric alcohols with hypervalent iodine reagents in the presence of iodine.[5] Presumably, the reaction proceeds through an alkyl hypoiodite intermediate.[6] The alkoxy radical subsequently undergoes a *β*-fragmentation to give a C2 radical, which in the great majority of cases is oxidized with an excess of the reagent to an oxycarbenium ion (Scheme 1, path a).[5f] This ion may participate in a number of inter- and intramolecular reactions to give modified carbohydrates with one less carbon.[5]

An alternative approach to this alkoxy radical fragmentation (ARF) was then considered, and it was envisioned that if the generation of the alkoxy radical is achieved under reductive conditions, the reaction may have different synthetic possibilities (Scheme 1, path b).

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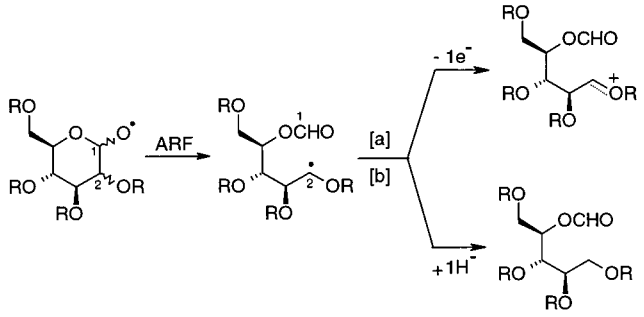
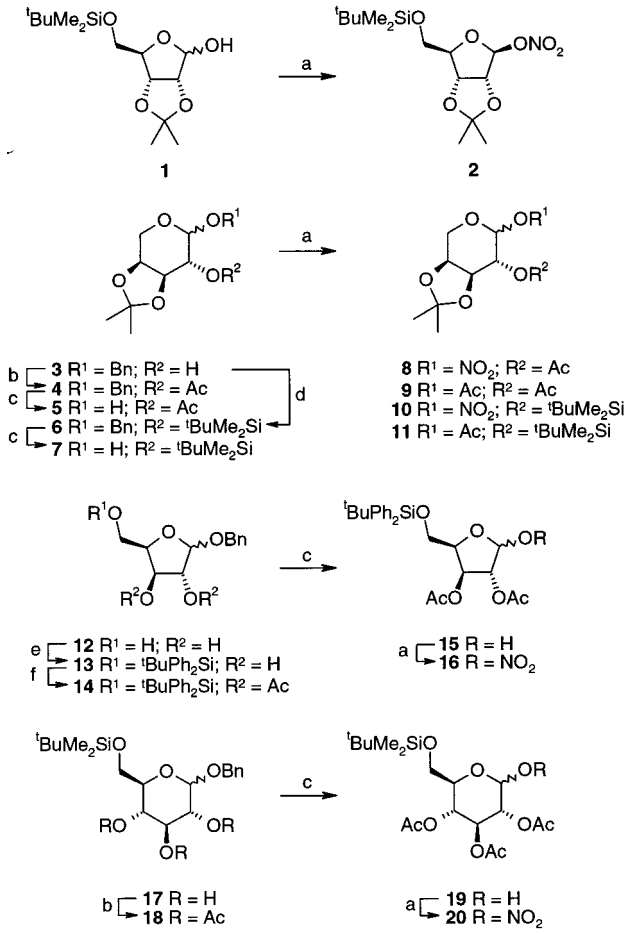
Scheme 1



At the time this work was initiated, several methods to prepare alcohol derivatives, precursors of alkoxy radicals, under these conditions were available. However, it soon became apparent that most of them, although very efficient to generate the O-radical, were unsuitable from a preparative point of view. Thus, hypohalogenites,[7] nitrite esters,[8] *O*-arylsulfenates,[9] and *N*-alkoxypyridine-2(1*H*)-thiones[10] were in general too unstable to be of any practical use. We decided that anomeric nitrate esters were at least in these primary steps of the study the only possible solution to this problem.[11] Since the work of Binkley and Koholic, nitrate esters[11f] have been used as alkoxy radical promoters under tri-*n*-butyltin hydride/AIBN conditions. Moreover, we were encouraged because at least two examples of anomeric nitrate esters (2,3,4,5-tetra-*O*-acetyl-1-*O*-nitro-D-glucopyranose[12] and 1,2:5,6-di-*O*-isopropylidene-1-*O*-nitro-D-mannofuranose[13]) were known at that time, and they seem to have substantial stability and can be easily handled at room temperature. Subsequently, we have also used *N*-phthalimido glycosides to generate anomeric alkoxy radicals. The reduction of *N*-alkoxyphthalimides with tri-*n*-butyltin hydride/AIBN to give alcohols has been described previously.[14] It is also known that *N*-acyloxyphthalimides can be transformed into alkyl chlorides by photosensitized chlorodecarboxylation[15] or into alkanes by reduction with tri-*n*-butyltin hydride/AIBN.[16] Both reactions occur through an O-radical intermediate.

Scheme 2[a]



[a] Key: (a) Ac_2O, fuming HNO_3, 0 °C; (b) Ac_2O, py, rt; (c) H_2, Pd/C, EtOAc, rt; (d) $^tBuMe_2SiCl$, imidazole, DMF, rt; (e) $^tBuPh_2SiCl$, imidazole, DMF, rt, 1 h, 88%; (f) Ac_2O, py, *N*,*N*-(dimethylamino)pyridine, rt, 2 h, 92%.

Results and Discussion

Here, we report on an application of the ARF methodology under reductive conditions to carbohydrates that is particularly effective for the synthesis of alditols having one less carbon. The necessary glycopyran-1-*O*-yl and glycofuran-1-*O*-yl radicals are generated by reaction of 1-*O*-nitro and 1-*O*-phthalimido derivatives of carbohydrates with tri-*n*-butyltin hydride in the presence of AIBN. In previous communications, we described the preliminary results obtained,[17] and we now disclose herein the full details of these experiments. The scope of the reaction was tested in substrates of the pentose and hexose series of carbohydrates, both in pyranose and furanose forms as depicted in Schemes 2 and 3.

Synthesis of Nitrate Esters. Although tetra-*O*-acetyl-1-*O*-nitro-D-glucopyranose has been known since 1901,[12b] the preparation of other 1-*O*-nitrocarbohydrate derivatives is limited to a few examples.[13,18] Reports on their exploitation as synthetic intermediates are also

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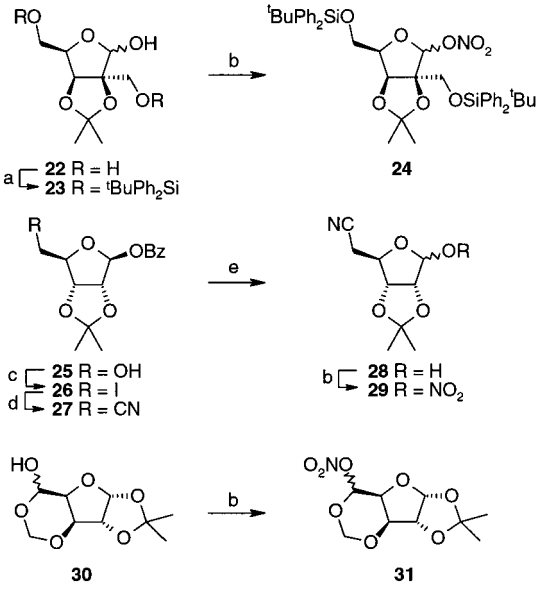
Scheme 3[a]

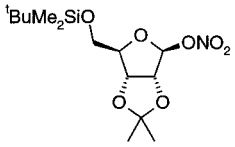
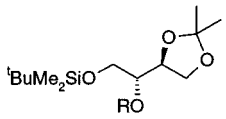
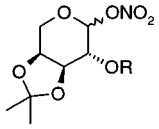
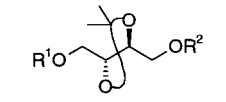
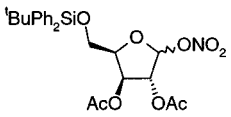
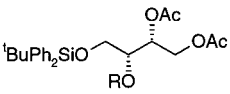
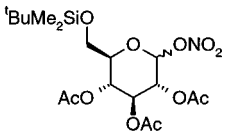
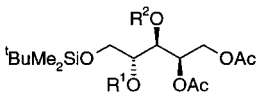
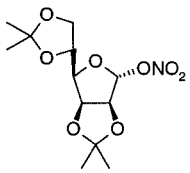
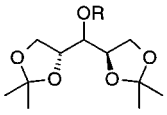


[a] Key: (a) ^{t}BuPh$_2$SiCl, imidazole, DMF, rt; (b) Ac$_2$O, fuming HNO$_3$, 0 °C; (c) PPh$_3$, I$_2$, imidazole, PhH, reflux, 10 min, 95%; (d) NaCN, DMSO, rt, overnight, 58%; (e) NaOMe, MeOH, −15 °C, 4 h, 86%.

rather scarce in the literature.[19] The conditions used for the synthesis of nitrate esters from alcohols are rather harsh, mixtures of nitric and sulfuric acids and nitric acid or dinitrogen pentoxide in chloroform often being employed. In this paper, we have demonstrated that anomeric alcohols of carbohydrates can easily be converted into the corresponding nitrate esters by a simple modification of the method of Honeyman, fuming nitric acid in acetic anhydride. Under these reaction conditions, acid-sensitive protecting groups such as isopropylidene, *tert*-butyldimethylsilyl or *tert*-butyldiphenylsilyl ethers survive and yields of 60−80% are normally obtained, the 1-*O*-acetyl derivative is the only side product observed. On the other hand, this reagent is not compatible with easily oxidized or highly acid-sensitive substrates such as benzyl, *p*-methoxybenzyl, and sensitive silyl ethers. The starting alcohols **1**, **5**, **7**, **15**, and **19** were prepared from readily available carbohydrates using well-established methods as shown in Scheme 2. The nitrate esters **2**, **16**, and **20** were synthesized using the above-mentioned methodology in the yields stated in Table 1 (entries 1, 4, and 5). These compounds are stable enough to be purified by quick chromatography and stored in the refrigerator. Nitrate esters **8** and **10** were unstable, although they can be purified by chromatography with substantial loss of material by hydrolysis (Table 1, entries 2 and 3). Nitrate **21** is a known stable compound prepared by nitration of 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose[13] (Table 1, entry 6).

To further test the scope and stereoselectivity of the ARF reaction, we prepared a number of nitrate esters of compounds possessing modified carbohydrate skeletons (Scheme 3). Disilylation with *tert*-butyldiphenylsilyl chloride and imidazole of the known triol **22**[20] followed by nitration gave the nitrate ester **24** in 93% yield as a mixture of anomers with a ratio of 1:3. The 5-cyanoribofuranoside **29** was prepared from alcohol **25**,[5e] after iodination of the primary alcohol, treatment with NaCN in DMSO, deprotection of the anomeric alcohol and nitration. Compound **30**, obtained in a single step from oxidative degradation of 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose,[21] was nitrated analogously at the hemiacetal alcohol to give nitrate ester **31** in good yield.

Table 1. Synthesis of Alditols by Alkoxy Radical Fragmentation of Anomeric Nitrate Esters[a]

entry	substrate	nBu$_3$SnH[b] (mmol)	time (h)	product	yield (%)
1[d]	 **2** (85%)	9	4	 **32a** R = CHO **b** R = H	79 16
2[d]	 **8** R = OAc	6	0.5	 **33a** R^1 = OAc; R^2 = CHO **b** R^1 = OAc; R^2 = H	75[e] 16
3[c]	**10** R = ^{t}BuMe$_2$Si			**34a** R^1 = ^{t}BuMe$_2$Si; R^2 = CHO **b** R^1 = ^{t}BuMe$_2$Si; R^2 = H	33[f] 18
4[c]	 **16** (56%)	9	1.5	 **35a** R = CHO **b** R = H	58 16
5[d]	 **20** (81%)	9	2	 **36a** R^1 = CHO; R^2 = Ac **b** R^1 = H; R^2 = Ac **c** R^1 = Ac; R^2 = H	83 12
6[c]	 **21** (86%)	7	2	 **37a** R = CHO **b** R = H	58 38

[a] The reactions were performed in dry PhH at reflux temperature under nitrogen. [b] mmol of n-Bu$_3$SnH per mmol of substrate. [c] Method A. [d] Method B. [e] Pure compound **8** was used. [f] Crude compound **10** was used.

Alkoxy Radical Fragmentation Reaction from Nitrate Esters. The ARF methodology was applied to carbohydrate derivatives of the pentose and hexose series in pyranose or furanose form as can be observed in Table 1. The optimization of the reaction conditions was established with readily accessible D-ribofuranosyl nitrate **2**. A good yield of D-erythritol derivative **32** (89%) was

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obtained when the reaction was carried out with tri-*n*-butyltin hydride (9 mmol) and AIBN (0.4 mmol) per mmol of **2** at reflux temperature in dry benzene under nitrogen (method A). The ratio between formate and hydrolyzed alcohol **32a**/**32b** was 1:4. The addition of pyridine (1 mmol) increased the overall ARF reaction yield to 95% and avoided formate hydrolysis, the **32a**/**32b** ratio now being approximately 4:1 (method B) (Table 1, entry 1). A number of reaction conditions were explored including decreasing the tri-*n*-butyltin hydride rate or increasing the amount of pyridine but all gave distinctly inferior results.

The use of *meso*-erythritol derivatives that have become asymmetric by substitution has attracted considerable attention from synthetic organic chemists as four carbon chiral synthons in enantiodivergent synthesis.[4] Taking this observation into account, we have prepared L-arabinopyranosyl nitrates **8** and **10** in order to prepare homochiral erythritol derivatives **33** and **34** with a very different substitution pattern from that of **32**.

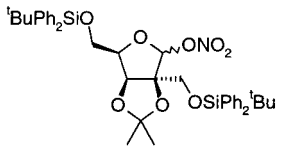
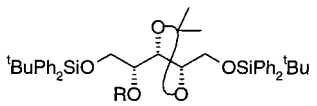
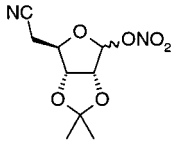
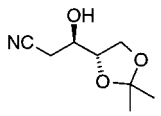
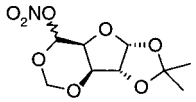
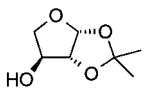
The reaction proceeded in good yield when pure chromatographed nitrate **8** was used as starting material (Table 1, entry 2), although, due to instability of the nitrate upon exposure to silica gel, the best overall yield (42%, two steps) of the fragmented compounds **33** was obtained by using crude **8** prepared immediately prior to use. A similar situation was observed during the ARF reaction of *tert*-butyldimethylsilyl ether **10**, the overall yield using crude nitrate being 51% (Table 1, entry 3). It is worth mentioning that, in some experiments, partial racemization of alcohol **33b** was detected. This process was probably due to a base- or acid-catalyzed transesterification reaction during the isolation or purification steps. To clarify the reaction mechanism, we performed hydrolysis of formate ester **33a** under various conditions and then analyzed the enantiomeric purity of the **33b** obtained in each case by converting it into its Mosher's ester.[22] The hydrolysis of formate **33a** with $NaHCO_3$ in MeOH at 0 °C led to **33b** (42%) with total racemization. When a solution of **33a** in wet MeOH was refluxed overnight, the optical purity of the alcohol **33b** obtained was determined to be 54% ee. Notwithstanding, the alcohol **33b** was obtained with 100% ee when the later experiment was modified by the use of recently dried MeOH.

D-Threitol derivatives **35**, which are also important four-carbon chiral synthons,[3] can be obtained by reductive fragmentation of the 1-*O*-nitro-D-xylofuranose derivative **16** as shown in entry 4 of Table 1.

To investigate further the scope of this reaction, we extended our studies to encompass carbohydrates of the hexose series (Table 1, entries 5 and 6). Thus, D-glucopyranosyl nitrate **20** and D-mannofuranosyl nitrate **21** were transformed into the D-arabinitol derivatives **36** and **37**, respectively, in excellent yields. This is an example of the potential interest of this reaction in the preparation of chiral synthons or chiral auxiliaries; two D-arabinitol derivatives possessing very different protection patterns were synthesized from easily accessible carbohydrates. As can be observed, the position of the readily hydrolyzable formate group depends only on the furanose or pyranose form of the starting carbohydrate.

(22) (a) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512−519. (b) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543−2549.

Table 2. Alkoxy Radical Fragmentation of Carbohydrate with Modified Skeletons[a]

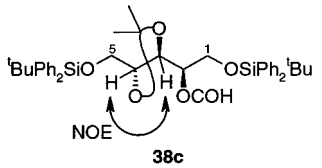
entry	substrate	nBu$_3$SnH[b] (mmol)	time (h)	product	yield (%)
1	 **24** (98%)	8	0.8	 **38a** R = CHO **b** R = H	81[c] 2
2	 **29** (92%)	9	14	 **39**	83
3	 **31** (65%)	9	5.5	 **40**	96

[a] The reactions were performed in dry PhH at reflux temperature under nitrogen using method A. [b] mmol of n-Bu$_3$SnH per mmol of substrate. [c] Arabinitol derivative **38c** (13%) is also obtained.

This feature may be of practical interest when the required alditols need further chemical transformations. The fragmentation reaction of compound **20** was realized under the conditions of method B, adding to the solution of n-Bu$_3$SnH/AIBN an equimolecular amount of pyridine. The reaction in the absence of base (method A) deserves some comment. Under these conditions a new alcohol **36c** is formed by intramolecular transesterification. The structures of alcohols **36b**,**c** were determined by NMR spectra, including DEPT, COSY, HMBC and HMQC experiments which permit unambiguous assignment of carbons and hydrogens. The transesterification mechanism was confirmed since both compounds **36a** and **36b** were transformed into **36c** when heated under reflux in wet MeOH.

A 2-C-branched-chain sugar nitrate **24** was used to investigate the stereoselectivity of the ARF reaction (Table 2, entry 1). The fragmentation−reduction of the C1−C2 bond proceeded preferentially with retention of configuration through the more stable transition state to give the D-xylitol derivative **38a**,**b** (83%). The less stable diastereoisomeric 1,5-di-*O*-(*tert*-butyldiphenyl)silyl-2-*O*-formyl-3,4-*O*-isopropylidene-D-arabinitol (**38c**)[23] was also obtained in 13% yield (dr, 6.7:1). The disposition trans (xylitol derivative) or cis (arabinitol derivative) of the two protons of the dioxolane ring was determined by intramolecular NOE experiments. Irradiation of H3 in the ^{1}H NMR spectrum of the D-arabinitol derivative **38c**[23]

(23) Arabinitol derivative **38c** obtained from the ARF reaction of nitrate **24**.



38c

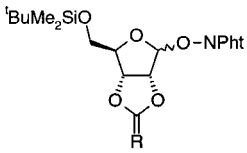
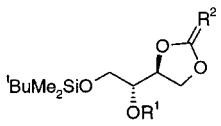
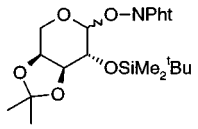
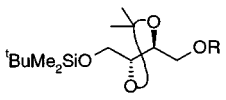
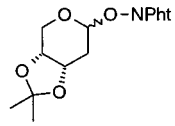
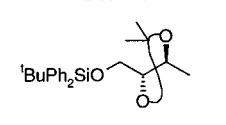
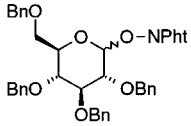
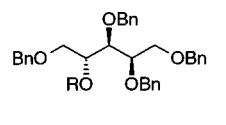
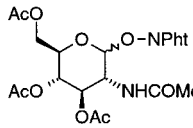
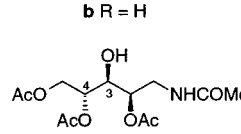
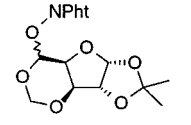
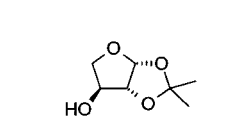
enhanced the H4 proton by 7%. Moreover, no NOE interaction was observed between the H2 and H3 protons in the spectrum of the D-xylitol derivative **38a**.

The 5-cyano-D-ribofuranoside **29** was synthesized with the goal of obtaining polyhydroxylated cyclopentanones by eventual intramolecular radical cyclization (Table 2, entry 2).[24] Unfortunately, **29** completely failed to undergo the desired ring closure upon treatment with *n*-Bu_3SnH/AIBN under various conditions. The sole product that could be isolated from these attempts was the 4-cyano-4-deoxy-D-erythritol derivative **39**. The best yield (83%) was achieved under the conditions summarized in Table 2. The high concentration of the reducing reagent necessary for the ARF reaction to take place apparently reduce the C2 radical before the cyclization reaction occurs. The reaction was also applied to the nitrate ester of a non anomeric hemiacetal, the dialdose **31**, as a method for the synthesis of 1,2-*O*-isopropylidene-*β*-L-threose (**40**), an interesting chiral building block in synthetic organic chemistry (Table 2, entry 3).[25] The reaction proceeded smoothly in 96% yield and may be one of the best protocols for the preparation of L-threose, requiring only three steps from the readily accessible and inexpensive 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose in 55% overall yield.

Alkoxy Radical Fragmentation Reaction from *N*-Phthalimido Glycosides. Although the ARF reactions described in Tables 1 and 2 proceeded satisfactorily in high yields, the formation of nitrate esters presents two major drawbacks: the incompatibility of the nitrating system with easily oxidized or highly acid-sensitive substrates and the instability observed in some cases. Thus, for example, nitrates **8** and **10** are easily hydrolyzed and substantial loss of material occurs during the isolation and purification steps (Table 1, entries 2 and 3). Some useful protective groups in carbohydrate chemistry are oxidized or hydrolyzed under these conditions (e.g. benzyl, *p*-methoxybenzyl, and sensitive silyl ethers). For example, we were unable to synthesize the nitrate ester of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose using this methodology. All this experimental evidence suggests that at least in some cases a more stable alkoxy radical precursor would be desirable. Therefore, an alternative and complementary approach to this methodology was explored using *N*-phthalimido glycosides. These compounds can be easily prepared by two general methods, from the corresponding alcohol and *N*-hydroxyphthalimide under Mitsunobu conditions[26] and from alkyl halides by displacement with the sodium salt of *N*-hydroxyphthalimide.[14] To prepare phthalimido glycosides we have used the Mitsunobu protocol as previously described.

The results of the ARF reaction using the system *n*-Bu_3SnH/AIBN are outlined in Table 3. The D-erythritol derivative **32** (Table 3, entry 1) was obtained in a somewhat lower yield compared to the fragmentation of nitrate ester **2** (Table 1, entry 1). The carbonate **42** was prepared in order to study the effect of a stronger electron-withdrawing group at C2 that should decrease the electron density at this position (Table 3, entry 2).[5f] A significantly better yield of the ARF reaction is obtained as compared to the fragmentation of the 2,3-isopropylidene derivative **41** (Table 3, entry 1). The preparation of the D-erythritol derivative **34** is better accomplished using this methodology (Table 3, entry 3) than that of the nitrate ester (Table 1, entry 3). The stable *N*-phthalimido L-arabinofuranoside **44** is more conveniently purified and handled than its homologous unstable nitrate **10**, and consequently, the yield can be substantially improved. The ARF of the 2-deoxy-D-

Table 3. Synthesis of Alditols by Alkoxy Radical Fragmentation of *N*-Phthalimido Glycosides[a]

entry	substrate	time (min)	product	yield (%)
1	 **41** R = Me, Me (97%)	30	 **32a** R^1 = CHO; R^2 = Me, Me **b** R^1 = H; R^2 = Me, Me	42 39
2	 **42** R = O (71%)	30	 **43a** R^1 = CHO; R^2 = O **b** R^1 = H; R^2 = O	48 49
3	 **44** (81%)	30	 **34a** R = CHO **b** R = H	64 31
4	**45** (54%)	35	**46**[b]	78
5	 **47** (69%)	30	 **48a** R = CHO **b** R = H	63 23
6	 **49** (72%)	240	 **50**	47
7	 **51** (65%)	105	 **40**	81-88

[a] The reactions were performed in dry PhH at reflux temperature under nitrogen containing *n*-Bu_3SnH (9 mmol) and AIBN (0.1 mmol) per mmol of substrate. [b] After the reaction was completed, imidazole was added and the mixture stirred at 80 °C for 1.5 h. After this, the reaction mixture was cooled to room temperature and more imidazole (4 mmol) and ^{t}BuPh$_2$SiCl (2 mmol) were added. The mixture was stirred for 1 h at this temperature. NPht- = phthalimido.

(24) (a) Tanner, D. D.; Rahimi, P. M.; *J. Org. Chem.* **1979**, *44*, 1674−1677. (b) Clive, D. L. J.; Beaulieu, P. L.; Set, L. *J. Org. Chem.* **1984**, *49*, 1313−1314.

(25) (a) Dhavale, D. D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *Tetrahedron Lett.* **1988**, *29*, 6163−6166. (b) Smith, A. B.; Sulikowski, G. A.; Sulikowski, M. M.; Fujimoto, K. *J. Am. Chem. Soc.* **1992**, *114*, 2567−2576. (c) Blackburn, G. M.; Rashid, A. *J. Chem. Soc., Chem. Commun.* **1988**, 317−319. (d) Wei, C. C.; De Bernardo, S.; Tengi, J. P.; Borgese, J.; Weigele, M. *J. Org. Chem.* **1985**, *50*, 3462−3467.

(26) (a) Mitsunobu, O. *Synthesis* **1981**, 1−28. (b) Grochowski, E.; Jurczak, J. *Synthesis* **1976**, 682−684. (c) Jurczak, J.; Grochowski, E. In *International Symposium on Phosphorus Chemistry Directed Towards Biology*; Burzenin, Poland, 1979; Stec, W. J., Ed.; Franklin Book Company: Philadelphia, 1980; p 54. (d) Grochowski, E.; Nashed, E. M.; Jurczak, J. *Bull. Pol. Acad. Sci. Chem.* **1987**, *35*, 255−260.

ribopyranose derivative **45** gave a volatile mixture of the expected alcohol and formate which was hydrolyzed in situ with imidazole and subsequently treated with *tert*-butyldiphenylsilyl chloride to give the 1-deoxy-D-erythritol derivative **46** in order not to lose material during the workup and purification steps.

N-Phthalimido D-glucosides **47** and **49** were prepared since all attempts to generate the homologous nitrate esters failed completely (Table 3, entries 5 and 6). Tetra-*O*-benzyl-D-arabinitol (**48**) was obtained in good yield but 1-acetamido-2,4,5-tri-*O*-acetyl-1-deoxy-D-arabinitol (**50**) was formed only in 47% yield. The only feasible mechanism for the formation of compound **50** involves the complete hydrolysis of the formate group and a subsequent intramolecular transesterification from the acetate at C3 to the alcohol at C4. The process is similar to that observed in the case of compound **36** (Table 1, entry 5). The complete hydrolysis of the formate, produced during the relatively long reaction time required for its completion, permits the acetyl transesterification. These side reactions are most likely responsible for the low yield observed. The 5-*O*-phthalimido-α-D-*xylo*-pentodialdo-1,4-furanose **51** was prepared in order to check the Mitsunobu reaction with a nonanomeric alcohol. The two isomeric *N*-phthalimido derivatives **51**-*R* and **51**-*S* were separately submitted to the ARF reaction, and the L-threose **40** was obtained in similar yields (Table 3, entry 7).

In conclusion, this ARF reaction permits the preparation of alditols with one carbon less from carbohydrates under reductive mild conditions. This is a convenient procedure for the synthesis of chiral polyhydroxylated four- and five-carbon building blocks for organic synthesis. The protocol proved to be extremely versatile, adaptable to a variety of carbohydrate skeletons, and compatible with numerous protective groups. The relative position of the readily hydrolyzable formyl group depends only on the pyranose or furanose form of the starting carbohydrate and may be very convenient when further transformations are required. Although precautions have to be taken with the use of HNO_3/Ac_2O mixtures, specially in scaled-up reactions (see general procedure), the nitrate method seems to us cheaper and more straightforward and is recommended when the ester is stable. Notwithstanding, the *N*-phthalimide glycoside methodology is more generally applicable.

Experimental Section

General Methods. Melting points were determined with a hot-stage apparatus and are uncorrected. Optical rotations were measured at the sodium line at ambient temperature in $CHCl_3$ solutions. IR spectra were recorded in $CHCl_3$ solutions unless otherwise stated. NMR spectra were determined at 500 MHz for ^1H and 125.7 MHz for ^{13}C in $CDCl_3$ unless otherwise stated, in the presence of TMS as internal standard. Mass spectra were determined at 70 eV. Merck silica gel 60 PF (0.063−0.2 mm) were used for column chromatography. Circular layers of 1 mm of Merck silica gel 60 PF_{254} were used on a Chromatotron for centrifugally assisted chromatography. Commercially available reagents and solvents were analytical grade or were purified by standard procedures prior to use.[27] All reactions involving air- or moisture-sensitive materials were carried out under a nitrogen atmosphere. The spray reagents for TLC analysis were conducted with 0.5% vanillin in H_2SO_4−EtOH (4:1) and further heating until development of color. Fuming nitric acid 100% (d = 1.52) was purchased from Fluka.

General Procedure for the Synthesis of the Nitrate Esters. A vigorously stirred solution of the alcohol (1 mmol) in Ac_2O (0.6 mL, 6.5 mmol) was treated with a solution of fuming nitric acid 100% (0.3 mL, 7.5 mmol) in Ac_2O (0.3 mL, 3.2 mmol) at 0 °C for 35−60 min (CAUTION: keep solutions of nitric acid and Ac_2O below room temperature; otherwise, vigorous exothermic decomposition may occur. Although when this precaution was observed the reactions occurred without incident, the use of a protective shield and a good hood is recommended). The reaction was quenched with a cooled saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic phase was washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The obtained residue was purified by chromatography under the conditions specified in each case. Full details of physical properties and spectroscopic data for compounds **2**, **8**, **16**, **20**, **21**, **24**, **29**, and **31** are given in the Supporting Information.

General Procedure for the Synthesis of *N*-Phthalimido Glycosides. DEAD (4 mmol) was added dropwise to a stirred solution of the alcohol (1 mmol), *N*-hydroxyphthalimide (4 mmol), and PPh_3 (4 mmol) in dry THF (11 mL), and the resulting solution was stirred at 0 °C for 1−2.5 h. The reaction was quenched with water and extracted with $CHCl_3$. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue obtained was purified by chromatography under the conditions specified in each case. Full details of physical properties, and spectroscopic data for compounds **41**, **42**, **44**, **45**, **47**, **49**, and **51** are given in the Supporting Information.

General Procedure for the Alkoxy Radical Fragmentation Reaction. Method A. A solution of nitrate or *N*-phthalimide glycoside (1 mmol) in dry benzene (10−17 mL) was heated to reflux with *n*-Bu_3SnH (7−9 mmol) and AIBN (0.2−0.4 mmol) for 1−5 h. After being cooled to room temperature, the solution was concentrated under reduced pressure. Two procedures were used to remove tin salts: (a) The reaction residue was treated with a saturated solution of potassium fluoride in CH_3CN, stirred for 20 min, and filtered over Celite and the filtrate concentrated under reduced pressure. (b) The residue was dissolved in CH_3CN and washed with *n*-hexane, and the combined more polar extracts were concentrated under reduced pressure. The residue obtained was purified by chromatography under the conditions specified in each case. **Method B.** To a stirred solution of the nitrate (1 mmol) in dry benzene (10−16 mL) were added under nitrogen *n*-Bu_3SnH (6−9 mmol), AIBN (0.2−0.4 mmol), and dry pyridine (1 mmol), and the mixture was heated to reflux for 0.5−4 h. Workup as in method A.

4-*O*-(*tert*-Butyldimethyl)silyl-3-*O*-formyl-1,2-*O*-isopropylidene-D-erythritol (32a) and 4-*O*-(*tert*-Butyldimethyl)-silyl-1,2-*O*-isopropylidene-D-erythritol (32b). Following the general procedure (method A), a solution of nitrate **2** (100 mg, 0.286 mmol) in dry benzene (3 mL) was heated to reflux with *n*-Bu_3SnH (702 μL, 2.61 mmol) and AIBN (20 mg, 0.12 mmol) for 4 h. Chromatotron chromatography (hexanes−EtOAc, 9:1) gave the formate **32a** (16 mg, 0.05 mmol, 17%) and the alcohol **32b** (59.2 mg, 0.21 mmol, 72%). Compound **32a**: oil; $[\alpha]_D$ −23.2 (c = 0.108); IR 2931, 1725, 1182 cm^{-1}; ^1H NMR 0.03 (6H, s), 0.86 (9H, s), 1.33 (3H, s), 1.38 (3H, s), 3.75 (1H, dd, J = 11.5, 5.0 Hz), 3.84 (1H, dd, J = 11.5, 3.3 Hz), 3.89 (1H, dd, J = 8.6, 6.3 Hz), 4.03 (1H, dd, J = 8.6, 6.5 Hz), 4.25 (1H, ddd, J = 6.1, 6.1, 6.1 Hz), 5.03 (1H, ddd, J = 5.3, 5.3, 3.4 Hz), 8.11 (1H, s); ^{13}C NMR (50.3 MHz) −5.5 (2 × CH_3), 18.2 (C), 25.2 (CH_3), 25.7 (3 × CH_3), 26.4 (CH_3), 62.0 (CH_2), 65.9 (CH_2), 74.1 (CH), 74.8 (CH), 109.3 (C), 160.4 (CH); MS m/z (rel intensity) (FAB) 305 (M^+ + H, 31), 289 (M^+ − CH_3, 54), 247 (100); HRMS calcd for $C_{13}H_{25}O_5Si$ 289.1471, found 289.1452. Anal. Calcd for $C_{14}H_{28}O_5Si$: C, 55.23; H, 9.27. Found: C, 55.10; H, 9.22. Compound **32b**: oil; $[\alpha]_D$ −1.3 (c = 0.08); IR 3563, 2931, 1256 cm^{-1}; ^1H NMR 0.08 (6H, s), 0.90 (9H, s), 1.34 (3H, s), 1.40 (3H, s), 2.50 (1H, d, J = 5.0 Hz), 3.59 (1H, m), 3.66 (1H, dd, J = 10.1, 5.4 Hz), 3.78 (1H, dd, J

(27) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

= 10.1, 3.6 Hz), 3.96−4.29 (2H), 4.07 (1H, dd, J = 11.9, 5.9 Hz); ^{13}C NMR −5.5 (2 × CH_3), 18.2 (C), 25.2 (CH_3), 25.8 (3 × CH_3), 26.6 (CH_3), 63.9 (CH_2), 66.7 (CH_2), 72.3 (CH), 75.6 (CH), 109.0 (C); MS *m/z* (rel intensity) 261 ($M^+ - CH_3$, 31), 219 (4), 161 (44), 131 (71); HRMS calcd for $C_{12}H_{25}O_4Si$ 261.1522, found 261.1521. Anal. Calcd for $C_{13}H_{28}O_4Si$: C, 56.48; H, 10.21 Found: C, 56.28; H, 10.23. Following the general procedure (method B), to a stirred solution of the nitrate **2** (100 mg, 0.286 mmol) in dry benzene (3 mL) were added under nitrogen *n*-Bu_3SnH (702 μL, 2.61 mmol), AIBN (20 mg, 0.12 mmol) and dry pyridine (23 μL, 0.29 mmol) and the mixture was heated to reflux for 4 h. Chromatotron chromatography (hexanes−EtOAc, 9:1) afforded the formate **32a** (65 mg, 0.21 mmol, 79%) and the alcohol **32b** (12.8 mg, 0.05 mmol, 16%).

4-*O*-Acetyl-1-*O*-formyl-2,3-*O*-isopropylidene-D-erythritol (33a) and 4-*O*-Acetyl-2,3-*O*-isopropylidene-D-erythritol (33b). Following the general procedure (method B), the nitrate **8** (25 mg, 0.09 mmol) was dissolved in dry benzene (1.5 mL) and heated to reflux with *n*-Bu_3SnH (0.145 mL, 0.54 mmol), AIBN (2.5 mg, 0.0152 mmol), and dry pyridine (7.3 μL, 0.09 mmol) for 30 min. Chromatotron chromatography (hexanes−EtOAc, 95:5 → 92:8) of the residue yielded the formate **33a** (15.7 mg, 0.07 mmol, 75%) and the alcohol **33b** (3 mg, 0.014 mmol, 16%). Compound **33a**: oil; $[\alpha]_D$ −3.5 (c = 1.58); IR 2990, 1730, 1094 cm^{-1}; ^{1}H NMR 1.39 (3H, s), 1.50 (3H, s), 2.11 (3H, s), 4.12 (1H, dd, J = 11.7, 6.3 Hz), 4.21 (1H, dd, J = 11.6, 6.4 Hz), 4.27 (1H, dd, J = 11.7, 4.7 Hz), 4.36 (1H, dd, J = 11.6, 4.1 Hz), 4.41 (1H, ddd, J = 6.3, 6.3, 4.7 Hz), 4.43 (1H, ddd, J = 6.4, 6.3, 4.1 Hz), 8.10 (1H, s); ^{13}C NMR (50.3 MHz) 20.8 (CH_3), 25.2 (CH_3), 27.7 (CH_3), 61.8 (CH_2), 62.3 (CH_2), 74.1 (CH), 74.4 (CH), 108.7 (C), 160.4 (CH), 170.6 (C); MS *m/z* (rel intensity) 217 ($M^+ - CH_3$, 100), 172 (2), 129 (8), 115 (44); HRMS calcd for $C_9H_{13}O_6$ 217.0712, found 217.0726. Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.72; H, 6.94. Found: C, 51.43; H, 7.28. Compound **33b**: oil; $[\alpha]_D$ +15.2 (c = 0.56) [lit.[2e] $[\alpha]_D$ +16.6 (c = 1.0)]; IR 3605, 2936, 1740, 1232 cm^{-1}; ^{1}H NMR 1.36 (3H, s), 1.47 (3H, s), 1.84 (1H, dd, J = 6.2, 6.2 Hz), 2.07 (3H, s), 3.67 (1H, ddd, J = 11.7, 6.2, 6.2 Hz), 3.74 (1H, ddd, J = 11.7, 6.2, 4.3 Hz), 4.12 (1H, dd, J = 11.7, 7.2 Hz), 4.26 (1H, dd, J = 11.7, 4.8 Hz), 4.28 (1H, ddd, J = 7.2, 6.2, 4.3 Hz), 4.36 (1H, ddd, J = 7.2, 7.2, 4.8 Hz); ^{13}C NMR 20.7 (CH_3), 25.0 (CH_3), 27.6 (CH_3), 60.9 (CH_2), 62.9 (CH_2), 74.5 (CH), 77.2 (CH), 109.0 (C), 170.6 (C); MS *m/z* (rel intensity) 189 ($M^+ - CH_3$, 32), 131 (32), 129 (32), 115 (95); HRMS calcd for $C_8H_{13}O_5$ 189.0763, found 189.0763. Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 52.70; H, 8.23. Alternatively the crude nitrate (300 mg) obtained in the previous reaction from compound **5** (300 mg, 1.29 mmol) was dissolved in dry benzene (10 mL) and heated to reflux with *n*-Bu_3SnH (1.55 mL, 5.76 mmol) and AIBN (30 mg, 0.18 mmol) for 30 min. Chromatotron chromatography of the residue (hexanes−EtOAc, 95:5 → 92:8) gave the formate **33a** (103.2 mg, 0.445 mmol, 34%), the alcohol **33b** (20.7 mg, 0.101 mmol, 8%), the acetate **9** (41.6 mg, 0.152 mmol, 12%) and alcohol **5** (62.1 mg, 0.268 mmol, 21%).

Hydrolysis of 4-*O*-Acetyl-2,3-*O*-isopropylidene-D-erythritol (33a). Method A. To a stirred solution of the formate **33a** (25 mg, 0.108 mmol) in MeOH (0.5 mL) at 0 °C was added a solution of sodium bicarbonate (13.4 mg, 0.16 mmol) in MeOH (1.5 mL). After 3 h at that temperature, the mixture was neutralized with acid resin (Dowex 50-X), filtered, and concentrated. The residue was purified by chromatotron chromatography (hexanes−EtOAc, 8:2 → 6:4) giving the compounds **33b** (9.2 mg, 0.05 mmol, 42%, 0%ee) and 2,3-*O*-isopropylideneerythritol **33c** (10.2 mg, 0.06 mmol, 58%). Compound **33c**: ^{1}H NMR (200 MHz) 1.37 (3H, s), 1.46 (3H, s), 2.78 (2H, br s), 3.75−3.80 (4H), 4.27−4.31 (2H). **Method B.** A solution of the formate **33a** (5 mg, 0.02 mmol) in MeOH Merck (0.2 mL) was heated to reflux overnight. Then the mixture was concentrated and the residue purified by chromatotron chromatography (hexanes−EtOAc, 7:3) to give the acetyl derivative **33b** (3.8 mg, 0.019 mmol, 86%, 54%ee). **Method C.** A solution of the formate **33a** (10 mg, 0.043 mmol) in dry MeOH (distilled over Na and collected over molecular sieves 4 Å) (0.43 mL) was heated to reflux for 4 h. Then the mixture was concentrated and the residue purified by chromatotron chromatography (hexanes−EtOAc, 7:3) to obtain the alcohol **33b** (5.6 mg, 0.03 mmol, 64%, 100%ee) and starting material **33a** (3.1 mg, 0.01 mmol, 31%). The enantiomeric excess of **33b** obtained by the different procedures, was determined by the ^{1}H NMR spectroscopic analysis of the Mosher esters.

Preparation and Analysis of Mosher Esters of 33b: 4-*O*-Acetyl-2,3-*O*-isopropylidene-1-*O*-[(*S*)-α-methoxyphenyl)]acetyl-D-erythritol and 1-*O*-Acetyl-2,3-*O*-isopropylidene-4-*O*-[(*S*)-α-methoxyphenyl)]acetyl-D-erythritol. A solution of **33b** (2.5 mg, 0.012 mmol), DCC (3.1 mg, 0.015 mmol), and (*S*)-(+)-α-methoxyphenylacetic acid (2.3 mg, 0.014 mmol) in dry CH_2Cl_2 (0.5 mL) was stirred at room temperature overnight. The reaction mixture was concentrated under reduced pressure and purified by chromatotron chromatography (hexanes−EtOAc, 7:3) to afford the Mosher esters. Compound 4-*O*-acetyl-2,3-*O*-isopropylidene-1-*O*-[(*S*)-α-methoxyphenyl)]acetyl-D-erythritol: ^{1}H NMR 1.33 (3H, s), 1.42 (3H, s), 2.06 (3H, s), 3.42 (3H, s), 3.93 (1H, m), 4.16−4.31 (4H), 4.82 (1H, s). Compound 1-*O*-acetyl-2,3-*O*-isopropylidene-4-*O*-[(*S*)-α-methoxyphenyl)]acetyl-D-erythritol: ^{1}H NMR 1.34 (3H, s), 1.45 (3H, s), 2.07 (3H, s), 3.42 (3H, s), 3.94 (1H, m), 4.13−4.31 (4H), 4.81 (1H, s). ^{1}H NMR analysis in $CDCl_3$ at 500 MHz focused on the isopropylidene methyls that are found in the region 1.33−1.45 ppm.

2-*O*-(*tert*-Butyldimethyl)silyl-3,4-*O*-isopropylidene-1-*O*-nitro-L-arabinopyranose (10). Following the general procedure, compound **7** (250 mg, 0.82 mmol) in Ac_2O (0.5 mL, 5.3 mmol) was treated with a solution of fuming nitric acid (0.25 mL, 6.2 mmol) in Ac_2O (0.25 mL, 2.7 mmol) at 0 °C for 45 min. The crude residue was used in the next reaction without further purification.

4-*O*-(*tert*-Butyldimethyl)silyl-1-*O*-formyl-2,3-*O*-isopropylidene-D-erythritol (34a) and 4-*O*-(*tert*-Butyldimethyl)-silyl-2,3-*O*-isopropylidene-D-erythritol (34b). Following the general procedure (method A), the crude **10** (320 mg) obtained from the previous reaction was dissolved in dry benzene (13.7 mL) and heated to reflux with *n*-Bu_3SnH (1.78 mL, 6.60 mmol) and AIBN (13.4 mg, 0.082 mmol) for 2 h. Column chromatography (hexanes−EtOAc, 98:2 → 9:1) afforded the formate **34a** (82.5 mg, 0.27 mmol, 33%), the alcohol **34b** (41 mg, 0.15 mmol, 18%), and the acetate **11** (98.3 mg, 0.28 mmol, 34%) as an anomeric mixture (α:β, 4:1), a byproduct in the formation of the nitrate **10**. Compound **34a**: oil; $[\alpha]_D$ −35.0 (c = 0.98); IR 2932, 1727, 1178 cm^{-1}; ^{1}H NMR 0.08 (6H, s), 0.90 (9H, s), 1.38 (3H, s), 1.47 (3H, s), 3.68−3.70 (2H), 4.21−4.25 (2H), 4.43 (1H, ddd, J = 6.5, 6.5, 3.0 Hz), 4.55 (1H, dd, J = 11.7, 3.0 Hz), 8.12 (1H, s); ^{13}C NMR ($CDCl_3$, 50.3 MHz) −5.6 (2 × CH_3), 18.1 (C), 24.5 (CH_3), 25.5 (3 × CH_3), 27.8 (CH_3), 61.3 (CH_2), 63.0 (CH_2), 75.1 (CH), 76.4 (CH), 109.1 (C), 160.7 (CH); MS *m/z* (rel intensity) 289 ($M^+ - CH_3$, 13), 247 (4), 229 (4), 219 (1), 189 (18), 143 (100); HRMS calcd for $C_{13}H_{25}O_5Si$ 289.1471, found 289.1446. Anal. Calcd for $C_{14}H_{28}O_5Si$: C, 55.23; H, 9.27. Found: C, 55.25; H, 9.57. Compound **34b**: oil; $[\alpha]_D$ −2.6 (c = 0.87); IR 3500, 2990, 1167 cm^{-1}; ^{1}H NMR 0.11 (3H, s), 0.12 (3H, s), 0.91 (9H, s), 1.36 (3H, s), 1.42 (3H, s), 3.00 (1H, dd, J = 8.4, 5.6 Hz), 3.69 (1H, dd, J = 10.6, 4.0 Hz), 3.76 (1H, ddd, J = 11.7, 8.4, 5.8 Hz), 3.78 (1H, dd, J = 10.6, 6.0 Hz), 3.82 (1H, ddd, J = 11.7, 5.8, 5.6 Hz), 4.23 (1H, ddd, J = 6.0, 6.0, 4.0 Hz), 4.35 (1H, ddd, J = 6.0, 5.8, 5.8 Hz); ^{13}C NMR ($CDCl_3$, 125.8 MHz) −5.7 (CH_3), −5.6 (CH_3), 18.1 (C), 25.1 (CH_3), 25.7 (3 × CH_3), 27.7 (CH_3), 60.6 (CH_2), 61.5 (CH_2), 76.7 (CH), 76.8 (CH), 108.3 (C); MS *m/z* (rel intensity) 261 ($M^+ - CH_3$, 40), 245 (9), 187 (10), 161 (58); HRMS calcd for $C_{12}H_{25}O_4Si$ 261.1522, found 261.1526. Anal. Calcd for $C_{13}H_{28}O_4Si$: C, 56.48; H, 10.21. Found: C, 56.31; H, 10.44. Compound **11**: white crystalline solid; IR 2931, 1745, 1142 cm^{-1}; ^{1}H NMR 0.09 (3H, s), 0.10 (3H, s), 0.13 (3H, s), 0.15 (3H, s), 0.88 (18H, s), 1.38 (6H, s), 1.54 (6H, s), 2.11 (6H, s), 3.75 (1H, dd, J = 7.2, 7.2 Hz), 3.88−3.93 (2H), 3.99 (1H, d, J = 13.2 Hz), 4.05−4.12 (3H), 4.18 (1H, dd, J = 6.3, 6.3 Hz), 4.26−4.28 (2H), 5.46 (1H, d, J = 7.0 Hz), 6.05 (1H, d, J = 3.5 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) −5.0 (CH_3), −4.8 (CH_3), −4.7 (CH_3), −4.5 (CH_3), 17.9 (C), 18.1 (C), 20.9 (2 × CH_3) 25.6 (6 × CH_3), 25.9 (2 × CH_3), 27.7 (CH_3), 27.8 (CH_3), 61.4 (CH_2), 63.6 (CH_2), 69.9 (2 ×

CH), 72.7 (CH), 72.8 (CH), 75.9 (CH), 79.0 (CH), 91.5 (CH), 92.7 (CH), 109.2 (C), 109.2 (C), 169.2 (C), 170.4 (C); MS *m*/*z* (rel intensity) 331 ($M^+ - CH_3$, 9), 289 (3), 287 (11), 229 (15); HRMS calcd for $C_{15}H_{27}O_6Si$ 331.1577, found 331.1561. Anal. Calcd for $C_{16}H_{30}O_6Si$: C, 55.46; H, 8.73. Found: C, 55.27; H, 8.98.

1,2-Di-*O*-acetyl-4-*O*-(*tert*-butyldiphenyl)silyl-3-*O*-formyl-D-threitol (35a) and 1,2-Di-*O*-acetyl-4-*O*-(*tert*-butyldiphenyl)silyl-D-threitol (35b). Following the general procedure (method A), the nitrate **16** (15 mg, 0.029 mmol) in dry benzene (0.5 mL) was heated to reflux with *n*-Bu_3SnH (70 μL, 0.261 mmol) and AIBN (2 mg, 0.012 mmol) for 1.5 h. The residue was purified by chromatotron chromatography (hexanes−EtOAc, 95:5) giving the formate **35a** (8 mg, 0.017 mmol, 58%), the alcohol **35b** (2.1 mg, 0.005 mmol, 16%) and compound **15** (2.6 mg, 0.005 mmol, 19%). Compound **35a**: oil; $[\alpha]_D$ +17.2 (*c* = 0.25); IR 2959, 1732, 1240 cm^{-1}; ^1H NMR 1.07 (9H, s), 1.96 (3H, s), 2.00 (3H, s), 4.07 (1H, dd, *J* = 11.4, 5.7 Hz), 4.12 (1H, ddd, *J* = 5.7, 4.4, 3.9 Hz), 4.16 (1H, dd, *J* = 11.9, 6.6 Hz), 4.21 (1H, dd, *J* = 11.4, 3.9 Hz), 4.42 (1H, dd, *J* = 11.9, 3.7 Hz), 5.15 (1H, ddd, *J* = 6.6, 4.4, 3.7 Hz), 7.38−7.42 (4H), 7.44−7.48 (2H), 7.68 (4H, d, *J* = 6.6 Hz), 7.77 (1H, s); ^{13}C NMR 19.3 (C), 20.6 (CH_3), 20.7 (CH_3), 26.8 (3 × CH_3), 62.0 (CH_2), 63.8 (CH_2), 69.6 (CH), 71.5 (CH), 127.6 (2 × CH), 127.7 (2 × CH), 129.9 (CH), 130.0 (CH), 132.6 (C), 132.9 (C), 135.7 (4 × CH), 160.2 (CH), 169.2 (C), 170.4 (C) MS *m*/*z* (rel intensity) 415 ($M^+ - C_4H_9$, 52), 327 (6), 309 (5), 267 (19); HRMS calcd for $C_{21}H_{23}O_7Si$ 415.1213, found 415.1204. Anal. Calcd. for $C_{25}H_{32}O_7Si$: C, 63.54; H, 6.82. Found: C, 63.66; H, 7.01. Compound **35b**: oil; $[\alpha]_D$ −18.3 (*c* = 0.40); IR 3686, 2962, 1739, 1113 cm^{-1}; ^1H NMR 1.07 (9H, s), 1.71 (3H, s), 2.00 (3H, s), 2.49 (1H, d, *J* = 7.3 Hz), 3.81 (1H, dddd, *J* = 7.3, 7, 5.6, 3.2 Hz), 3.95 (1H, ddd, *J* = 6.6, 4.6, 3.2 Hz), 4.07 (1H, dd, *J* = 11.7, 4.6 Hz), 4.11 (1H, dd, *J* = 11.4, 5.6 Hz), 4.12 (1H, dd, *J* = 11.7, 6.6 Hz), 4.17 (1H, dd, *J* = 11.4, 7.0 Hz), 7.38−7.48 (6H), 7.64 (2H, d, *J* = 6.7 Hz), 7.71 (2H, d, *J* = 6.7 Hz); ^{13}C NMR (50.3 MHz) 19.4 (C), 20.4 (CH_3), 20.8 (CH_3), 27.0 (3 × CH_3), 65.0 (2 × CH_2), 70.2 (CH), 71.0 (CH), 127.5 (2 × CH), 127.89 (2 × CH), 129.8 (CH), 130.2 (CH), 132.2 (C), 133.4 (C), 135.5 (2 × CH), 135.9 (2 × CH), 170.5 (C), 170.9 (C); MS *m*/*z* (rel intensity) 429 ($M^+ - CH_3$, <1), 387 (10), 327 (14), 267 (56); HRMS calcd for $C_{23}H_{29}O_6Si$ 429.1733, found 429.0798. Anal. Calcd for $C_{24}H_{32}O_6Si$: C, 64.84; H, 7.25. Found: C, 64.90; H, 7.39.

1,2,3-Tri-*O*-acetyl-5-*O*-(*tert*-butyldimethyl)silyl-4-*O*-formyl-D-arabinitol (36a), 1,2,3-Tri-*O*-acetyl-5-*O*-(*tert*-butyldimethyl)silyl-D-arabinitol (36b), and 1,2,4-Tri-*O*-acetyl-5-*O*-(*tert*-butyldimethyl)silyl-D-arabinitol (36c). Following the general procedure (method A), nitrate derivative **20** (80 mg, 0.172 mmol) in dry benzene (3 mL) was heated to reflux with *n*-Bu_3SnH (0.42 mL, 1.548 mmol) and AIBN (8 mg, 0.049 mmol) for 2 h. Chromatotron chromatography (hexanes−EtOAc, 95:5 → 92:8) of the residue afforded the formate **36a** (23.8 mg, 0.06 mmol, 33%) and the alcohols **36b** (16.3 mg, 0.04 mmol, 24%) and **36c** (26.3 mg, 0.07 mmol, 39%). Compound **36a**: oil; $[\alpha]_D$ +30.0 (*c* = 0.20); IR 3031, 1744, 1047 cm^{-1}; ^1H NMR 0.03 (3H, s), 0.02 (3H, s), 0.86 (9H, s), 2.02 (3H, s), 2.05 (3H, s), 2.09 (3H, s), 3.66 (1H, dd, *J* = 11.2, 5.2 Hz), 3.76 (1H, dd, *J* = 11.2, 4.1 Hz), 4.00 (1H, dd, *J* = 11.8, 6.6 Hz), 4.26 (1H, dd, *J* = 11.8, 4.9 Hz), 5.16 (1H, ddd, *J* = 7.2, 5.2, 4.1 Hz), 5.38 (1H, ddd, *J* = 6.6, 4.9, 3.5 Hz), 5.43 (1H, dd, *J* = 7.2, 3.5 Hz), 7.98 (1H, s); ^{13}C NMR −5.7 (2 × CH_3), 18.1 (C), 20.5 (2 × CH_3), 20.6 (CH_3), 25.6 (3 × CH_3), 61.1 (CH_2), 62.0 (CH_2), 68.4 (CH), 68.6 (CH), 70.5 (CH), 159.6 (CH), 169.4 (C), 170.0 (C), 170.4 (C); MS *m*/*z* (rel intensity) 405 ($M^+ - CH_3$, 2), 363 (72), 275 (15), 117 (100); HRMS calcd for $C_{17}H_{29}O_9Si$ 405.1581, found 405.1539. Anal. Calcd for $C_{18}H_{32}O_9Si$: C, 51.41; H, 7.67. Found: C, 51.10; H, 7.67. Compound **36b**: oil; $[\alpha]_D$ +26.0 (*c* = 0.20); IR 3548, 2930, 1744, 1372 cm^{-1}; ^1H NMR 0.03 (3H, s), 0.04 (3H, s), 0.87 (9H, s), 2.01 (3H, s), 2.07 (3H, s), 2.09 (3H, s), 2.70 (1H, d, *J* = 2.3 Hz), 3.51 (1H, dd, *J* = 10.0, 5.1 Hz), 3.63 (1H, dd, *J* = 10.0, 3.4 Hz), 3.68 (1H, dddd, *J* = 8.3, 5.1, 3.4, 2.3 Hz), 4.00 (1H, dd, *J* = 11.6, 7.0 Hz), 4.25 (1H, dd, *J* = 11.6, 5.1 Hz), 5.10 (1H, dd, *J* = 8.3, 2.9 Hz), 5.50 (1H, ddd, *J* = 7.0, 5.1, 2.9 Hz); ^{13}C NMR −5.6 (2 × CH_3), 18.2 (C), 20.6 (2 × CH_3), 20.7 (CH_3), 25.7 (3 × CH_3), 62.3 (CH_2), 63.0 (CH_2), 69.27 (CH), 69.33 (CH), 70.5 (CH), 169.7 (C), 170.2 (C), 170.4 (C); MS *m*/*z* (rel intensity) 335 ($M^+ - C_4H_9$, 8), 275 (24), 259 (2), 215 (6); HRMS calcd for $C_{13}H_{23}O_8Si$ 335.1162, found 335.1165. Anal. Calcd for $C_{17}H_{32}O_8Si$: C, 52.02; H, 8.22. Found: C, 51.88; H, 8.60. Compound **36c**: oil; $[\alpha]_D$ +9.0 (*c* = 0.20); IR 3550, 2993, 1748, 1140 cm^{-1}; ^1H NMR 0.05 (6H, s), 0.88 (9H, s), 2.02 (3H, s), 2.03 (3H, s), 2.05 (3H, s), 3.01 (1H, d, *J* = 5.6 Hz), 3.77 (1H, dd, *J* = 10.9, 5.1 Hz), 3.89 (1H, dd, *J* = 10.9, 4.1 Hz), 4.05 (1H, ddd, *J* = 9.0, 5.6, 2.0 Hz), 4.16 (1H, dd, *J* = 11.6, 7.4 Hz), 4.39 (1H, dd, *J* = 11.6, 5.1 Hz), 4.79 (1H, ddd, *J* = 9.0, 5.1, 4.1 Hz), 5.23 (1H, ddd, *J* = 7.4, 5.1, 2.0 Hz); ^{13}C NMR −5.7 (CH_3), −5.6 (CH_3), 18.1 (C), 20.7 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 25.7 (3 × CH_3), 62.6 (CH_2), 62.9 (CH_2), 69.3 (CH), 69.9 (CH), 70.7 (CH), 169.9 (C), 170.2 (C), 170.8 (C); MS *m*/*z* (rel intensity) 335 ($M^+ - C_4H_9$, 12), 275 (24), 233 (6), 215 (6); HRMS calcd for $C_{13}H_{23}O_8Si$ 335.1162, found 335.1167. Anal. Calcd for $C_{17}H_{32}O_8Si$: C, 52.02; H, 8.22. Found: C, 52.01; H, 8.47. Alternatively, and following the general procedure (method B), nitrate **20** (80 mg, 0.172 mmol) was dissolved in dry benzene (3 mL) and heated to reflux with *n*-Bu_3SnH (0.42 mL, 1.548 mmol), AIBN (8 mg, 0.049 mmol), and dry pyridine (14 μL, 0.172 mmol) for 2 h. Chromatotron chromatography (hexanes−EtOAc, 95:5 → 92:8) gave the formate **36a** (60.1 mg, 0.14 mmol, 83%) and the alcohol **36b** (7.8 mg, 0.02 mmol, 12%).

Hydrolysis of 1,2,3-Tri-*O*-acetyl-5-*O*-(*tert*-butyldimethyl)silyl-4-*O*-formyl-D-arabinitol (36a). A solution of the formate **36a** (5 mg, 0.01 mmol) in wet MeOH (0.25 mL) was heated to reflux for 6 h. Then the mixture was concentrated and the residue purified by chromatotron chromatography (hexanes−EtOAc, 92:8) to obtain the alcohol **36c** (2.1 mg, 0.005 mmol, 45%).

Transesterification of 1,2,3-Tri-*O*-acetyl-5-*O*-(*tert*-butyldimethyl)silyl-D-arabinitol (36b). A solution of **36b** (4.8 mg, 0.012 mmol) in wet MeOH (0.3 mL) was heated to reflux for 30 min. Then the mixture was concentrated and the residue purified by chromatotron chromatography (hexanes−EtOAc, 92:8) to give the alcohol **36c** (2.6 mg, 0.007 mmol, 54%).

3-*O*-Formyl-1,2:4,5-di-*O*-isopropylidene-D-arabinitol (37a) and 1,2:4,5-Di-*O*-isopropylidene-D-arabinitol (37b). Following the general procedure (method A), to compound **21** (80 mg, 0.26 mmol) in dry benzene (4.3 mL) were added *n*-Bu_3SnH (489 μL, 1.82 mmol) and AIBN (10 mg, 0.06 mmol), and the mixture was heated to reflux for 2 h. Chromatotron chromatography (hexanes−EtOAc, 95:5 → 92:8) of the residue gave the formate **37a** (39 mg, 0.15 mmol, 58%) and the alcohol **37b** (24.5 mg, 0.10 mmol, 38%). Compound **37a**: oil; $[\alpha]_D$ +19.7 (*c* = 0.178); IR 3018, 1728, 1175 cm^{-1}; ^1H NMR 1.36 (6H, s), 1.41 (3H, s), 1.43 (3H, s), 3.82 (1H, dd, *J* = 8.8, 6.2 Hz), 3.88 (1H, dd, *J* = 8.8, 6.2 Hz), 4.07 (1H, dd, *J* = 8.8, 6.2 Hz), 4.09 (1H, dd, *J* = 8.8, 6.2 Hz), 4.26 (1H, ddd, *J* = 6.2, 6.2, 6.2 Hz), 4.34 (1H, ddd, *J* = 6.2, 6.2, 4.3 Hz), 5.12 (1H, dd, *J* = 6.2, 4.3 Hz), 8.19 (1H, s) ^{13}C NMR 25.2 (CH_3), 25.3 (CH_3), 26.0 (CH_3), 26.5 (CH_3), 65.8 (CH_2), 66.3 (CH_2), 72.6 (CH), 74.6 (CH), 74.7 (CH), 109.6 (2 × C), 160.3 (CH); MS *m*/*z* (rel intensity) 245 ($M^+ - CH_3$, 71), 187 (100), 141 (10), 127 (11); HRMS calcd for $C_{11}H_{17}O_6$ 245.1025, found 245.1010. Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74. Found: C, 55.23; H, 7.87. Compound **37b**: oil; $[\alpha]_D$ −14.3 (*c* = 0.21); IR 3560, 2990, 1240, 1154 cm^{-1}; ^1H NMR 1.36 (3H, s), 1.39 (3H, s), 1.44 (3H, s), 1.45 (3H, s), 2.30 (1H, d, *J* = 6.4 Hz), 3.43 (1H, ddd, *J* = 7.7, 6.4, 4.3 Hz), 3.92 (1H, dd, *J* = 8.2, 6.7 Hz), 3.99 (1H, ddd, *J* = 7.7, 5.7, 5.7 Hz), 4.02 (1H, dd, *J* = 8.3, 5.7 Hz), 4.09 (1H, dd, *J* = 8.2, 6.7 Hz), 4.13 (1H, dd, *J* = 8.3, 5.7 Hz), 4.26 (1H, ddd, *J* = 6.7, 6.7, 4.3 Hz); ^{13}C NMR 25.1 (CH_3), 25.1 (CH_3), 26.3 (CH_3), 26.6 (CH_3), 66.1 (CH_2), 67.2 (CH_2), 72.5 (CH), 76.0 (CH), 76.1 (CH), 109.2 (C), 109.3 (C); MS *m*/*z* (rel intensity) 217 ($M^+ - CH_3$, 50), 159 (32), 101 (100); HRMS calcd for $C_{10}H_{17}O_5$ 217.1076, found 217.1075. Anal. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 56.74; H, 8.96.

Hydrolysis of 3-*O*-Formyl-1,2:4,5-di-*O*-isopropylidene-D-arabinitol (37a). A solution of the formate **37a** (9.3 mg, 0.036 mmol) in DBU (1 mL, 6.7 mmol) was stirred at room-temperature overnight. After concentration under reduced pressure, the residue was purified by chromatotron chroma-

tography (hexanes−EtOAc, 9:1), giving the alcohol **37b** (6.2 mg, 0.03 mmol, 75%).

1,5-Di-*O*-(*tert*-butyldiphenyl)silyl-4-*O*-formyl-2,3-*O*-isopropylidene-D-xylitol (38a), 1,5-Di-*O*-(*tert*-butyldiphenyl)silyl-2,3-*O*-isopropylidene-D-xylitol (38b), and 1,5-Di-*O*-(*tert*-butyldiphenyl)silyl-2-*O*-formyl-3,4-*O*-isopropylidene-D-arabinitol. Following the general procedure (method A), the nitrate **24** (100 mg, 0.135 mmol) was dissolved in dry benzene (3 mL) and heated to reflux with *n*-Bu_3SnH (290 μL, 1.08 mmol) and AIBN (10 mg, 0.06 mmol) for 50 min. Chromatotron chromatography (hexanes−EtOAc, 98:2 → 95:5) of the residue gave the formates 1,5-di-*O*-(*tert*-butyldiphenyl)silyl-2-*O*-formyl-3,4-*O*-isopropylidene-D-arabinitol (12.3 mg, 0.02 mmol, 13%) and **38a** (76.5 mg, 0.11 mmol, 81%) and the alcohol **38b** (2.1 mg, 0.003 mmol, 2%). 1,5-Di-*O*-(*tert*-butyldiphenyl)silyl-2-*O*-formyl-3,4-*O*-isopropylidene-D-arabinitol: oil; $[\alpha]_D$ −14.0 (*c* = 0.20); IR 2932, 1725, 1113 cm^{-1}; ^1H NMR 1.04 (9H, s), 1.07 (9H, s), 1.33 (3H, s), 1.34 (3H, s), 3.68 (1H, dd, *J* = 11.3, 5.5 Hz), 3.79 (1H, dd, *J* = 11.3, 5.5 Hz), 3.90 (1H, dd, *J* = 11.6, 5.2 Hz), 3.95 (1H, dd, *J* = 11.6, 2.5 Hz), 4.26 (1H, ddd, *J* = 5.5, 5.5, 5.5 Hz), 4.44 (1H, dd, *J* = 8.4, 5.5 Hz), 5.16 (1H, ddd, *J* = 8.4, 5.2, 2.5 Hz), 7.36−7.43 (12H), 7.66−7.70 (8H), 7.80 (1H, s); ^{13}C NMR 19.2 (2 × C), 25.2 (CH_3), 26.7 (3 × CH_3), 26.9 (3 × CH_3), 27.3 (CH_3), 62.5 (CH_2), 63.0 (CH_2), 72.6 (CH), 74.0 (CH), 77.6 (CH), 108.6 (C), 127.6−127.7 (8 × CH), 129.7 (4 × CH), 133.1 (2 × C), 133.2 (2 × C), 135.6−135.7 (8 × CH), 160.0 (CH); MS *m*/*z* (rel intensity) 681 (M^+ − CH_3, 4), 639 (6), 581 (8), 535 (33); HRMS calcd for $C_{40}H_{49}O_6Si_2$ 681.3068, found 681.3080. Anal. Calcd for $C_{41}H_{52}O_6Si_2$: C, 70.65; H, 7.52. Found: C, 70.50; H, 7.64. Compound **38a**: oil; $[\alpha]_D$ +13.0 (*c* = 0.20); IR 2932, 1732, 1177 cm^{-1}; ^1H NMR 1.03 (9H, s), 1.04 (9H, s), 1.33 (3H, s), 1.40 (3H, s), 3.65 (1H, dd, *J* = 11.2, 4.0 Hz), 3.80 (1H, dd, *J* = 11.2, 4.0 Hz), 3.86 (1H, dd, *J* = 11.5, 7.0 Hz), 3.91 (1H, dd, *J* = 11.5, 3.2 Hz), 4.00 (1H, ddd, *J* = 7.0, 4.0, 4.0 Hz), 4.31 (1H, dd, *J* = 7.0, 7.0 Hz), 5.16 (1H, ddd, *J* = 7.0, 7.0, 3.2 Hz), 7.34−7.43 (12H), 7.64−7.70 (8H), 7.92 (1H, s); ^{13}C NMR 19.17 (C), 19.21 (C), 26.7 (3 × CH_3), 26.8 (3 × CH_3), 27.1 (2 × CH_3), 62.6 (CH_2), 63.9 (CH_2), 74.7 (CH), 74.8 (CH), 79.5 (CH), 109.7 (C), 127.68−127.73 (8 × CH), 129.7−129.8 (4 × CH), 133.0 (2 × C), 133.1 (2 × C), 135.62−135.65 (8 × CH), 160.2 (CH); MS *m*/*z* (rel intensity) 681 (M^+ − CH_3, 2), 639 (6), 581 (17), 535 (15); HRMS calcd for $C_{40}H_{49}O_6Si_2$ 681.3068, found 681.3070. Anal. Calcd for $C_{41}H_{52}O_6Si_2$: C, 70.65; H, 7.52. Found: C, 70.65; H, 7.49. Compound **38b**: oil; $[\alpha]_D$ +10.0 (*c* = 0.44); IR 3583, 3071, 1073 cm^{-1}; ^1H NMR 1.06 (9H, s), 1.07 (9H, s), 1.33 (3H, s), 1.40 (3H, s), 2.71 (1H, d, *J* = 5.2 Hz), 3.70 (1H, m), 3.79−3.89 (4H), 4.08−4.13 (2H), 7.36−7.43 (12H), 7.68−7.72 (8H); ^{13}C NMR (50.3 MHz) 19.2 (C), 19.3 (C), 26.79 (CH_3), 26.81 (6 × CH_3), 27.2 (CH_3), 64.4 (CH_2), 65.1 (CH_2), 73.5 (CH), 76.4 (CH), 80.6 (CH), 109.2 (C), 127.7 (8 × CH), 129.8 (4 × CH), 133.2 (4 × C), 135.6 (8 × CH); MS *m*/*z* (rel intensity) 653 (M^+ − CH_3, 4), 611 (1), 553 (1), 535 (20); HRMS calcd for $C_{39}H_{49}O_5Si_2$ 653.3119, found 653.3113. Anal. Calcd for $C_{40}H_{52}O_5Si_2$: C, 71.81; H, 7.83. Found: C, 72.02; H, 7.90.

Hydrolysis of 1,5-Di-*O*-(*tert*-butyldiphenyl)silyl-4-*O*-formyl-2,3-*O*-isopropylidene-D-xylitol (38a). A solution of the formate **38a** (11.6 mg, 0.017 mmol) in MeOH (0.17 mL) was heated to reflux overnight. Then the mixture was concentrated and the residue purified by chromatotron chromatography (hexanes−EtOAc, 95:5) to give the alcohol **38b** (9.8 mg, 0.015 mmol, 88%).

4-Cyano-4-deoxy-1,2-*O*-isopropylidene-D-erythritol (39). Following the general procedure (method A), to compound **29** (100 mg, 0.41 mmol) in dry benzene (5 mL) was added *n*-Bu_3SnH (1 mL, 3.69 mmol) and AIBN (10 mg, 0.061 mmol) and the mixture was heated to reflux overnight. Chromatotron chromatography (hexanes−EtOAc, 9:1) afforded the alcohol **39** (58.6 mg, 0.34 mmol, 83%) and the lactol **28** (6 mg, 0.03 mmol, 7%). Compound **39**: oil; $[\alpha]_D$ +12.1 (*c* = 1.0); IR 3612, 2254, 1602, 1068 cm^{-1}; ^1H NMR 1.32 (3H, s), 1.39 (3H, s), 2.55 (1H, dd, *J* = 16.9, 7.4 Hz), 2.70 (1H, dd, *J* = 16.9, 4.0 Hz), 3.84 (1H, ddd, *J* = 7.4, 7.1, 4.0 Hz), 3.94 (1H, dd, *J* = 8.4, 4.8 Hz), 3.99 (1H, ddd, *J* = 7.1, 6.1, 4.8 Hz), 4.09 (1H, dd, *J* = 8.4, 6.1 Hz); ^{13}C NMR 22.9 (CH_2), 24.8 (CH_3), 26.6 (CH_3), 66.2 (CH_2), 68.7 (CH), 77.1 (CH), 109.8 (C), 117.4 (C); MS *m*/*z* (rel intensity) 172 (M^+ + H, 1), 156 (100), 101 (75); HRMS calcd for $C_8H_{14}NO_3$ 172.0974, found 172.0989. Anal. Calcd for $C_8H_{13}NO_3$: C, 56.13; H, 7.65; N, 8.18. Found: C, 56.46; H, 7.68; N, 7.85. Acetylation of **39** (21 mg, 0.12 mmol) in dry pyridine (1.2 mL, 0.015 mmol) and Ac_2O (0.4 mL, 4.2 mmol) at room temperature for 4 h gave after Chromatotron chromatography (hexanes−EtOAc, 9:1) 3-*O*-acetyl-4-cyano-4-deoxy-1,2-*O*-isopropylidene-D-erythritol (24.2 mg, 0.11 mmol, 92%): oil; $[\alpha]_D$ −44.3 (*c* = 0.20); IR 2256, 1755, 1061 cm^{-1}; ^1H NMR 1.36 (3H, s), 1.40 (3H, s), 2.11 (3H, s), 2.77 (1H, dd, *J* = 17.3, 5.0 Hz), 2.84 (1H, dd, *J* = 17.3, 4.4 Hz), 3.78 (1H, dd, *J* = 9.0, 4.7 Hz), 4.08 (1H, dd, *J* = 9.0, 6.4 Hz), 4.22 (1H, ddd, *J* = 7.8, 6.4, 4.7 Hz), 4.84 (1H, ddd, *J* = 7.8, 5.0, 4.4 Hz); ^{13}C NMR 19.9 (CH_2), 20.7 (CH_3), 24.8 (CH_3), 26.5 (CH_3), 66.5 (CH_2), 69.3 (CH), 74.6 (CH), 110.4 (C), 116.0 (C), 169.7 (C); MS *m*/*z* (rel intensity) 198 (M^+ − CH_3, 100), 115 (12), 101 (47); HRMS calcd for $C_9H_{12}NO_4$ 198.0766, found 198.0772. Anal. Calcd for $C_{10}H_{15}NO_4$: C, 56.33; H, 7.09; N, 6.57. Found: C, 56.37; H, 7.21; N, 6.47.

1,2-*O*-Isopropylidene-*β*-L-threose (40). Following the general procedure (method A), a solution of nitrate **31** (60 mg, 0.23 mmol) in dry benzene (4 mL) was heated to reflux with *n*-Bu_3SnH (0.56 mL, 2.07 mmol) and AIBN (6 mg, 0.04 mmol) for 5.5 h. Chromatotron chromatography (hexanes−EtOAc, 7:3) gave the title compound **40** (35 mg, 0.22 mmol, 96%): mp 84−85 °C (from *n*-hexane); $[\alpha]_D$ +13.4 (*c* = 0.8); IR 3467, 2993, 1163, cm^{-1}; ^1H NMR (200 MHz) 1.32 (3H, s), 1.49 (3H, s), 3.88 (1H, dd, *J* = 10.1, 0.8 Hz), 4.10 (1H, dd, *J* = 10.1, 2.3 Hz), 4.26 (1H, dd, *J* = 2.3, 0.8 Hz), 4.50 (1H, d, *J* = 3.6 Hz), 5.96 (1H, d, *J* = 3.6 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 26.2 (CH_3), 26.7 (CH_3), 72.9 (CH_2), 75.2 (CH), 84.9 (CH), 105.2 (CH), 111.8 (C); MS *m*/*z* (rel intensity) 159 (M^+ − 1, 1), 145 (80), 127 (27), 102 (4), 85 (100); HRMS calcd for $C_7H_{11}O_4$ 159.065734, found 159.065662. Anal. Calcd for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.54; H, 7.54.

4-*O*-(*tert*-Butyldimethyl)silyl-3-*O*-formyl-1,2-*O*-isopropylidene-D-erythritol (32a) and 4-*O*-(*tert*-Butyldimethyl)-silyl-1,2-*O*-isopropylidene-D-erythritol (32b). Following the general procedure (method A), to a solution of **41-**α (107 mg, 0.238 mmol) in dry benzene (3.6 mL) were added, under nitrogen, *n*-Bu_3SnH (0.576 mL, 2.142 mmol) and AIBN (4 mg, 0.024 mmol) and the solution was heated to reflux for 30 min. Chromatotron chromatography (hexanes−EtOAc, 95:5) afforded the formate **32a** (30.2 mg, 0.099 mmol, 42%) and the alcohol **32b** (25.6 mg, 0.093 mmol, 39%) identical to those previously described (vide supra).

4-*O*-(*tert*-Butyldimethyl)silyl-3-*O*-formyl-1,2-*O*-(oxomethylene)-D-erythritol (43a) and 4-*O*-(*tert*-Butyldimethyl)silyl-3-*O*-formyl-1,2-*O*-(oxomethylene)-D-erythritol (43b). Following the general procedure (method A), to a solution of the carbonate **42-**α (94 mg, 0.216 mmol) in dry benzene (3.24 mL) were added *n*-Bu_3SnH (523 μL, 1.944 mmol) and AIBN (3.6 mg, 0.022 mmol), and the solution was heated to reflux for 30 min. Chromatotron chromatography (hexanes−EtOAc, 9:1) afforded the formate **43a** (30 mg, 0.103 mmol, 48%) and the alcohol **43b** (28 mg, 0.107 mmol, 49%). Data compound for **43a** and **43b** were identical to those given by us previously.[5f]

4-*O*-(*tert*-Butyldimethyl)silyl-1-*O*-formyl-2,3-*O*-isopropylidene-D-erythritol (34a) and 4-*O*-(*tert*-Butyldimethyl)-silyl-2,3-*O*-isopropylidene-D-erythritol (34b). Following the general procedure (method A), a solution of the anomeric mixture **44** (103 mg, 0.229 mmol) in dry benzene (3.4 mL) was heated to reflux with *n*-Bu_3SnH (554 μL, 2.061 mmol) and AIBN (3.8 mg, 0.023 mmol) for 30 min. Chromatotron chromatography of the residue (hexanes−EtOAc, 95:5) afforded the formate **34a** (45 mg, 0.148 mmol, 64%) and the alcohol **34b** (20 mg, 0.072 mmol, 31%).

4-*O*-(*tert*-Butyldiphenyl)silyl-1-deoxy-2,3-*O*-isopropylidene-D-erythritol (46). Following the general procedure (method A), to a solution of the anomeric mixture **45** (200 mg, 0.627 mmol) in dry benzene (10 mL) were added, under nitrogen, *n*-Bu_3SnH (1.52 mL, 5.64 mmol) and AIBN (10.3 mg, 0.063 mmol), and the solution was stirred at reflux temperature for 30 min. Then the mixture was cooled, and imidazole (85 mg, 1.25 mmol) was added. After the mixture was stirred

for 1.5 h at 80 °C, it was cooled to room temperature, and *tert*-butyldiphenylsilyl chloride (326 μL, 1.25 mmol) and more imidazole (171 mg, 2.51 mmol) were added. The reaction mixture was stirred for another 1 h, concentrated, dissolved in CH_3CN and washed with *n*-hexane. The combined more polar extracts were concentrated under reduced pressure to give a residue, which was purified by flash column chromatography (hexanes−EtOAc, 96:4) to yield compound **46** (188 mg, 0.489 mmol, 78%): oil; $[\alpha]_D$ +7.1 (c = 0.990); IR (film) 2932, 1379, 1113 cm^{-1}; ^1H NMR 1.06 (9H, s), 1.33 (3H, d, J = 6.5 Hz), 1.34 (3H, s), 1.38 (3H, s), 3.66 (1H, dd, J = 10.4, 4.8 Hz), 3.73 (1H, dd, J = 10.4, 7.9 Hz), 4.17 (1H, ddd, J = 7.8, 5.8, 4.9 Hz), 4.39 (1H, dddd, J = 6.4, 6.4, 6.4, 6.4 Hz), 7.39−7.44 (6H), 7.66−7.69 (4H); ^{13}C NMR (50.3 MHz) 14.9 (CH_3), 19.2 (C), 25.5 (CH_3), 26.6 (3 × CH_3), 28.1 (CH_3), 62.5 (CH_2), 73.2 (CH), 77.8 (CH), 107.6 (C), 127.7 (4 × CH), 129.7 (2 × CH), 133.2 (C), 133.4 (C), 135.5 (4 × CH); MS *m*/*z* (rel intensity) (FAB) 383 (M^+ + H, 2), 369 (M^+ − CH_3, 13), 327 (27), 269 (100); HRMS calcd for $C_{22}H_{29}O_3Si$ 369.1886, found 369.1880. Anal. Calcd for $C_{23}H_{32}O_3Si$: C, 71.83; H, 8.39. Found: C, 72.01; H, 8.54.

1,2,3,5-Tetra-*O*-Benzyl-4-*O*-formyl-D-arabinitol (48a) and 1,2,3,5-Tetra-*O*-Benzyl-D-arabinitol (48b). Following the general procedure (method A), to a stirred solution of the anomeric mixture **47** (103 mg, 0.150 mmol) in dry benzene (2.25 mL) were added, under nitrogen, *n*-Bu_3SnH (363 μL, 1.35 mmol) and AIBN (2.5 mg, 0.015 mmol), and the solution was heated to reflux for 35 min. Chromatotron chromatography (hexanes−EtOAc, 95:5 → 9:1) afforded the formate **48a** (51 mg, 0.094 mmol, 63%) and the alcohol **48b** (18 mg, 0.035 mmol, 23%). Compound **48a**: foam; $[\alpha]_D$ −12.9 (c = 0.975); IR (film) 1727 cm^{-1}; ^1H NMR 3.60 (1H, dd, J = 9.8, 6.1 Hz), 3.65 (1H, dd, J = 9.8, 5.4 Hz), 3.75 (1H, dd, J = 11.0, 5.8 Hz), 3.78 (1H, ddd, J = 5.8, 5.8, 3.9 Hz), 3.82 (1H, dd, J = 11.0, 2.9 Hz), 3.94 (1H, dd, J = 5.9, 3.8 Hz), 4.43 (1H, d, J = 12.0 Hz), 4.46 (2H, s), 4.49 (1H, d, J = 12.0 Hz), 4.53 (1H, d, J = 11.6 Hz), 4.57 (1H, d, J = 11.4 Hz), 4.63 (1H, d, J = 10.4 Hz), 4.65 (1H, d, J = 11.4 Hz), 5.31 (1H, ddd, J = 5.8, 5.8, 2.8 Hz), 7.22−7.35 (20H), 7.94 (1H, s); ^{13}C NMR (50.3 MHz) 68.3 (CH_2), 69.4 (CH_2), 72.7 (CH), 73.1 (2 × CH_2), 73.4 (CH_2), 74.6 (CH_2), 77.4 (CH), 77.6 (CH), 127.6−128.4 (20 × CH), 137.1 (C), 137.9 (2 × C), 138.0 (C), 160.4 (C); MS *m*/*z* (rel intensity) (EI, 70 eV) 449 (M^+ - Bn, 1), 357 (1), 341 (1), 91 (100); HRMS calcd for $C_{27}H_{29}O_6$ 449.1964, found 449.1998. Anal. Calcd for $C_{34}H_{36}O_6$: C, 75.53; H, 6.71. Found: C, 75.73; H, 6.97. Compound **48b**: oil; $[\alpha]_D$ −1.3 (c = 0.395); IR (film) 3468, 3031, cm^{-1}; ^1H NMR 2.89 (1H, d, J = 5.4 Hz), 3.59 (1H, dd, J = 10.0, 5.5 Hz), 3.62 (1H, dd, J = 10.0, 3.5 Hz), 3.65−3.70 (2H), 3.71 (1H, dd, J = 7.5, 3.0 Hz), 3.95 (1H, ddd, J = 5.5, 5.5, 3.5 Hz), 3.99 (1H, dddd, J = 9.0, 9.0, 5.0, 5.0 Hz), 4.46 (1H, d, J = 12.0 Hz), 4.48 (1H, s), 4.50 (1H, s), 4.52 (1H, d, J = 12.0 Hz), 4.53 (2H, s), 4.62 (1H, d, J = 11.7 Hz), 4.71 (1H, d, J = 11.6 Hz), 7.21−7.34 (20H); ^{13}C NMR (50.3 MHz) 69.0 (CH_2), 69.6 (CH_2), 70.4 (CH_2), 72.4 (CH_2), 72.6 (2 × CH_2), 72.9 (CH_2), 77.0 (CH), 77.1 (CH), 127.7−128.3 (20 × CH), 138.1 (2 × C), 138.2 (2 × C); MS *m*/*z* (rel intensity) (EI, 70 eV) 421 (M^+ − Bn, 1), 315 (1), 253 (2), 91 (100); HRMS calcd for $C_{26}H_{29}O_5$ 421.2015, found 421.2053. Anal. Calcd for $C_{33}H_{36}O_5$: C, 77.32; H, 7.08. Found: C, 77.57; H, 7.23.

1-Acetamido-2,4,5-tri-*O*-acetyl-1-deoxy-D-arabinitol (50). Following the general procedure (method A), a solution of the anomeric mixture **49** (50 mg, 0.102 mmol) in dry benzene (1.53 mL) was heated to reflux with *n*-Bu_3SnH (247 μL, 0.918 mmol) and AIBN (1.7 mg, 0.01 mmol) for 4 h. Chromatotron chromatography of the residue (hexanes−EtOAc, 1:9) yielded the alcohol **50** (15.4 mg, 0.048 mmol, 47%): mp 117−118.5 °C (from ethyl acetate−*n*-hexane); $[\alpha]_D$ +21.7 (c = 0.410); IR (film) 3322, 1747, 1743, 1716, 1660 cm^{-1}; ^1H NMR 1.98 (3H, s), 2.01 (3H, s), 2.03 (3H, s), 2.04 (3H, s), 3.12 (1H, ddd, J = 14.0, 5.5, 5.4 Hz), 3.73 (1H, br d, J = 9.3 Hz), 3.79 (1H, ddd, J = 14.1, 8.7, 8.7 Hz), 4.26 (1H, dd, J = 12.3, 5.2 Hz), 4.47 (1H, dd, J = 12.3, 2.5 Hz), 4.60 (1H, d, J = 3.8 Hz), 4.80 (1H, ddd, J = 8.8, 5.4, 1.6 Hz), 5.08 (1H, ddd, J = 9.5, 5.3, 2.4 Hz), 6.15 (1H, dd, J = 6.5, 6.5 Hz); ^{13}C NMR (50.3 MHz) 20.6 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 23.0 (CH_3), 38.8 (CH_2), 63.3 (CH_2), 67.3 (CH), 69.5 (CH), 70.2 (CH), 169.8 (C), 171.0 (2 × C), 172.3 (C); MS *m*/*z* (rel intensity) (FAB) 342 (M^+ + Na, 100), 320 (M^+ + H, 40). Anal. Calcd for $C_{13}H_{21}NO_8$: C, 48.90; H, 6.63; N, 4.39. Found: C, 48.62; H, 6.68; N, 4.21.

Reduction of (5*R*)-1,2-*O*-Isopropylidene-3,5-*O*-methylene-5-*O*-phthalimido-α-D-*xylo*-pentodialdo-1,4-furanose (51-*R*) and (5*S*)-1,2-*O*-Isopropylidene-3,5-*O*-methylene-5-*O*-phthalimido-α-D-*xylo*-pentodialdo-1,4-furanose (51-*S*). Following the general procedure (method A), to a stirred solution of the isomer **51**-*R* (42 mg, 0.116 mmol) in dry benzene (1.74 mL) were added *n*-Bu_3SnH (280 μL, 1.044 mmol) and AIBN (1.9 mg, 0.012 mmol), and the solution was heated to reflux for 1 h and 45 min. Chromatotron chromatography (hexanes−EtOAc, 7:3) afforded the compound **40** (15 mg, 0.094 mmol, 81%). Data identical to those described above. Alternatively, to a stirred solution of the isomer **51**-*S* (76 mg, 0.209 mmol) in dry benzene (3.13 mL) were added *n*-Bu_3SnH (506 μL, 1.88 mmol) and AIBN (3.4 mg, 0.021 mmol) and the solution was heated to reflux for 1 h and 45 min. Chromatotron chromatography (hexanes−EtOAc, 7:3) afforded the compound **40** (29.4 mg, 0.184 mmol, 88%). Data were identical to those described above.

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Supporting Information Available: Experimental procedures, physical properties, and spectroscopic data for compounds **2**, **4**−**9**, **12**−**16**, **18**−**21**, **23**, **24**, **26**−**29**, **31**, **41**, **42**, **44**, **45**, **47**, **49**, and **51**. This material is available free of charge via the Internet at http://pubs.acs.org.

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