(2 in. × 100 cm) with 2 N acetic acid. The main peptide containing portion of this column (in two batches of ~100/mg each) was then purified on a Waters Delta Prep. 3000 Preparative LC using a PrepPak reverse-phase C_{18} column (57 mm × 30 cm, 15–20 μm particle size, 300-Å pore size). A gradient of 15–30% B over 90 min at a flow rate of 100 mL/min (buffer A = 95% H_2O, 5% CH_3CN, 0.1% TFA; buffer B = 100% CH_3CN, 0.1% TFA) was used. Individual fractions were analyzed for purity by HPLC on a Spectra Physics 8000B LC using a C_4 4.2 mm × 10 cm, 5 μm particle size, 300-Å pore size column, 20% B to 35% A over 30 min.

Fractions containing ≥99.5% pure product by integration were combined, lyophilized, and then sent for further analysis.

Analytical Methods. Amino Acid Analysis. Amino acid analysis was performed under standard conditions on a Beckman System 6300. The amino acid analysis of Synthetic I is as follows [(theoretical):actual]. Lys(3):3.01; His(3):2.97; Arg(2):1.95, Asx(3):3.05; Ser(3):2.92; Glx(5):5.03; Gly(1):0.99; Val(2):1.99; Ile(1):0.95; Leu(4):4.12; Tyr(1):1.00; Phe(1):0.99; Nle(2):2.08.

Peptide Mapping. Two nanomoles of the peptide were digested with trypsin (100:1 by weight, in 0.02 M $NaHCO_3$, pH 8.5) at 37 °C for 4 h. The digest was immediately injected onto a Vydac C18 reverse-phase column, 150 × 4.6 mm equilibrated with 0.1% trifluoroacetic acid in water at 40 °C. The tryptic peptides were eluted with a linear gradient of 0–50% CH_3CN containing 0.1% TFA over 30 min at a flow rate of 1.5 mL per minute. The peaks of absorption at 210 nM were collected, and amino acid analyses were performed after 20-h acid hydrolyses.

NMR Spectroscopy. NMR spectra were obtained on a Varian XL-400 MHz spectrometer at ambient temperature with approximately 0.5 mM peptide. Chemical shifts are relative to internal deuteriated TSP (sodium 3-(trimethylsilyl)propionate-*2,2,3,3-d*$_4$). Suppression of the water signal was carried out by the WEFT sequence.[6]

FAB Mass Spectroscopy. The samples were analyzed by FAB-MS on a Finnigan-MAT No. 731 mass spectrometer fitted with an Ion Tek FAB gun by using xenon bombardment gas. Accelerating voltage was reduced from the normal 8 kV to 3 kV and resolution was set at R = 1000. Spectra were acquired in an SS 200 data system, and centroids of (M + H) peak clusters were interpolated between cesium iodide cluster ions to determine their masses.

Stereoselectivity in Electrophile-Mediated Intramolecular Cyclizations of Hept-2-enitols

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Electrophile (dibromine, diiodine, benzeneselenenyl chloride, and mercuric acetate) mediated intramolecular cyclization of (*Z*)-7-*O*-benzyl-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (**9**) gives predominantly 2,5-anhydro-1-*O*-benzyl-6,7-dideoxy-6-substituted-3,4-*O*-isopropylidene-D-*glycero*-L-*allo*-heptitol while electrophile-mediated intramolecular cyclization of (*E*)-7-*O*-benzyl-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (**11**) gives predominantly 3,6-anhydro-7-*O*-benzyl-1,2-dideoxy-2-substituted-4,5-*O*-isopropylidene-D-*glycero*-D-*gluco*-heptitol. The synthesis of D-*ribo*-hept-2-enitols **9** and **11** and the stereochemical and mechanistic aspects of their electrophile-mediated intramolecular cyclizations are discussed. The proposed Hehre reactivity model for electrophilic addition reactions to prochiral alkenes bearing an allylic oxygen predicts the stereochemical outcome of these kinetically controlled cyclizations.

Introduction

Since the pioneering work of Sinäy and coworkers,[1] electrophile-mediated cyclizations have been used in the formation of α- and β-2-deoxyhexapyranosides,[2] 6-deoxy-D-*xylo*-hex-5-enosides,[3] *C*-ribofuranosides,[4-7] *C*-arabinofuranosides,[8-10] *C*-nucleosides,[11-13] and natural products such as *N*-acetylneuraminic acid.[14] In the cases where five-membered rings (furan derivatives **2** and **4**) are formed from electrophilic attack onto an unsubstituted terminal olefin (**1** and **3**) and subsequent trapping by the internal nucleophile, there is usually an enrichment of the epimer in which H-2 and H-3 on the newly formed heterocycle are cis.[4-6,8-10] This results in the stereoselective formation of the α epimer of heterocycle **2** and the β epimer of heterocycle **4** (eq 1, 2). However, Mann and Kane[11] achieved excellent stereocontrol with ethyl (*Z*)-7-*O*-benzyl-2,3-dideoxy-4,5-*O*-isopropylidene-2-methyl-D-*ribo*-hept-2-enoate (**5**) to give solely the β epimer during the synthesis of showdomycin (eq 3). Freeman and Robarge[7] reported similar results with ethyl (*Z*)-7-*O*-benzyl-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enoate (**7a**) and suggested that the origin of this β-selectivity in **5** may be due to a severe steric interaction in one conformer that is absent in the other (eq 4).[12]

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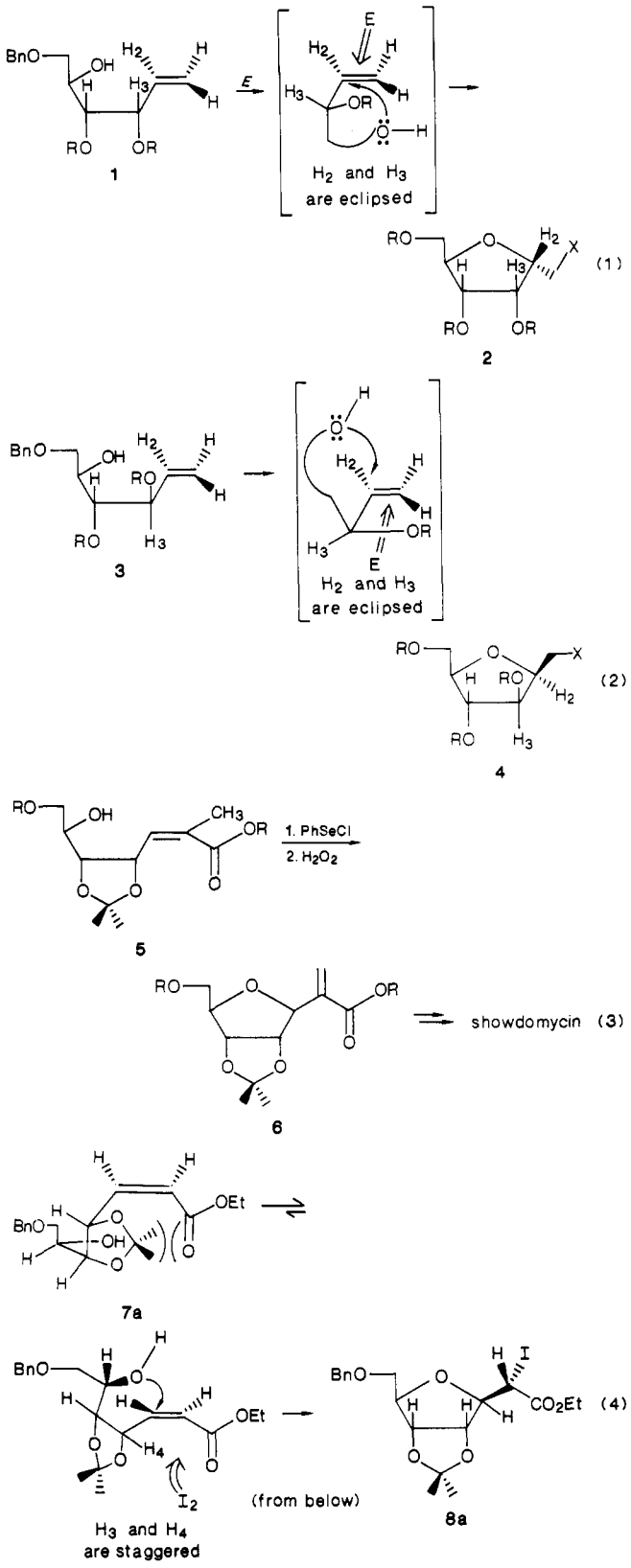
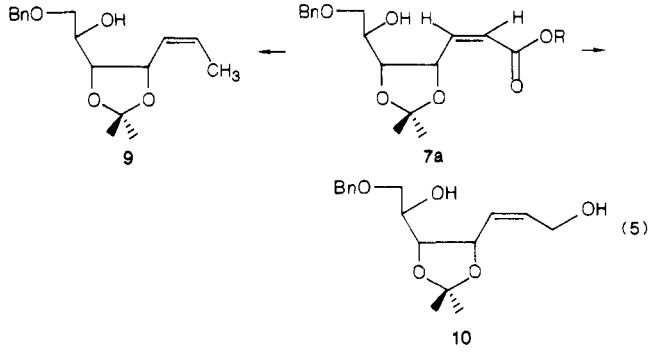


Owing to our long-standing interest in the mechanisms of electrophilic and nucleophilic addition reactions to carbon–carbon double bonds and carbon–carbon triple bonds,[15] and encouraged by the β-selectivities shown with esters **5** and **7a**, it was decided to investigate the use of a *Z*-substituted double bond to achieve β-selective intramolecular cyclizations. A simple *Z*-alkyl substituted (i.e. CH_3) olefin was chosen to probe the contribution of possible inductive and steric effects on β-selectivity.[16] In the absence of severe steric effects, a methyl-substituted double bond is expected to be more reactive toward an electrophile relative to (*Z*)-hept-2-enoate **5** or **7a**. Thus, the reaction may proceed faster and in higher yield with excellent β-selectivity. This would also allow a study of some of the factors governing the regiochemistry of ring closure (i.e., substituted furans versus substituted pyrans).

Results and Discussion

Many of the starting materials for this study were synthesized by known chemical procedures. Ethyl (*Z*)-7-*O*-benzyl-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enoate (**7a**)[7,11] was successively silylated (to ethyl (*Z*)-7-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enoate, **7b**),[17] reduced to (*Z*)-7-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (**7c**),[18] converted to an allylic chloride [(*Z*)-7-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-1-chloro-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol, **7d**],[19] reduced (to (*Z*)-7-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol, **7e**),[20] and deprotected to give (*Z*)-7-*O*-benzyl-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (**9**) in 39% overall yield (eq 5).[21] Reduction of ester **7a** gave (*Z*)-7-*O*-benzyl-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (**10**).[18,22]



Isomerization of **7b** to ethyl (*E*)-7-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enoate (**7f**),[7] followed by reduction to (*E*)-7-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (**7g**),[18] allylic chlorination to (*E*)-7-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-1-chloro-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (**7h**),[19] reduction to (*E*)-7-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (**7i**),[20] and deprotection gave (*E*)-7-*O*-

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(16) As an *approximate* indicator of relative steric bulk, the *A* value for a methyl is 7.2 kJ/mol while that of a methyl ester is 5.31 kJ/mol. Testa, B. In *Principles of Stereochemistry*; Gassman, P. G., Ed.; Marcel Dekker, Inc., 1979.

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(21) Compound **7a** was chosen a starting material to synthesize **9** since conventional Wittig chemistry on the lactol 5-*O*-benzyl-2,3-*O*-isopropylidene-D-ribofuranose (2.0 equiv of $Ph_3PCH_2CH_3Br$, BuLi, THF, reflux) gave an inseparable mixture of **9** and **11** in a ratio of 1:4.

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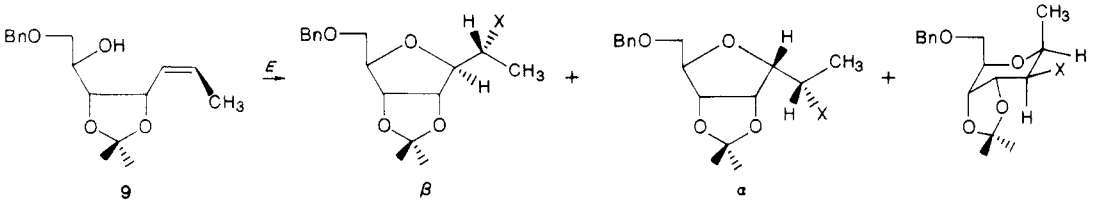
Table I. Electrophile-Mediated Intramolecular Cyclizations of (*Z*)-7-*O*-Benzyl-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (9)

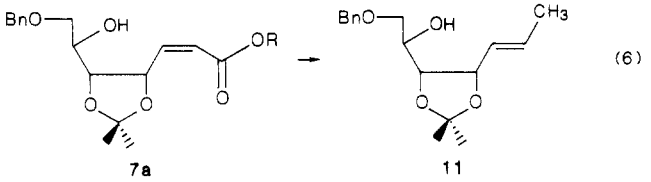


9 β α

electrophile	X	overall yield,[a] %	β	yield, %	α	yield, %	pyran derivative	yield, %
I_2	I	87	**14a**	54	**14b**	5	**14c**	28
NBS	Br	80	**15a**	66	**15b**	3	**15c**	11
$Hg(OAc)_2$	HgCl	85	**16a**	43	**16b**	18	**16c**	24[b]
PhSeCl	SePh	73	**17a**	18	**17b**	7		

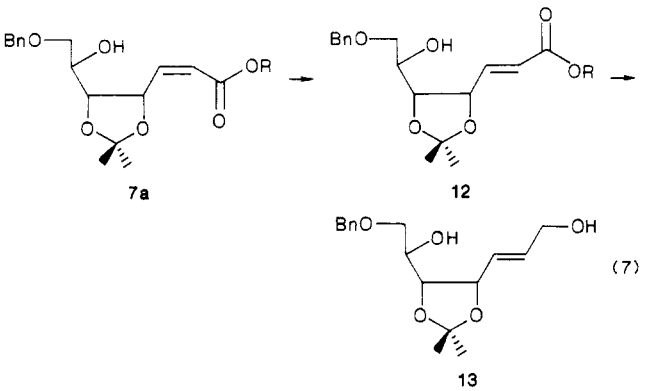
[a] Isolated yield. [b] The stereoselectivity of this cyclization was assessed by converting the crude organomercurial products into the iodo products by treatment with diiodine and ^1H NMR integration of the three sets of methyl doublets.

benzyl-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (**11**, 34%, eq 6).



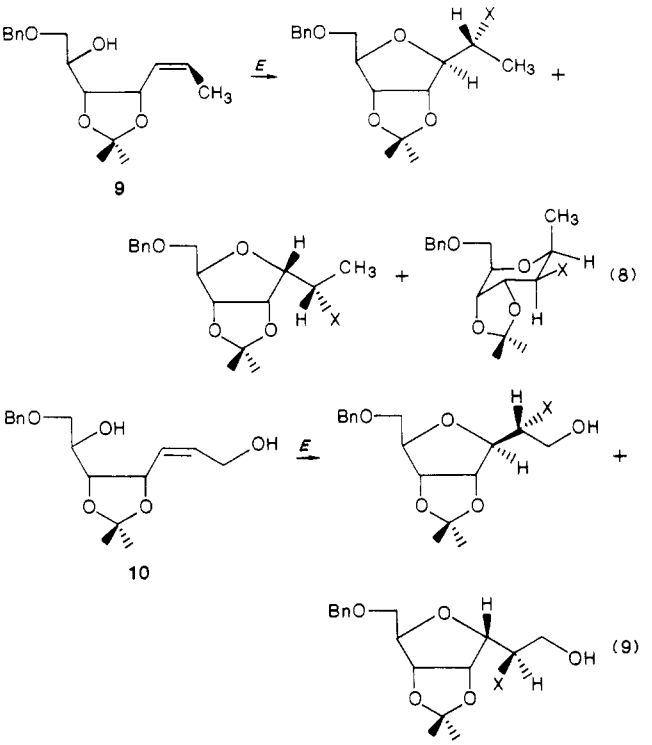
7a 11 (6)

Since the deprotection of **7f** with tetrabutylammonium fluoride in tetrahydrofuran gave a mixture of products, owing in part to a Michael addition reaction, ethyl (*E*)-7-*O*-benzyl-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enoate (**12**) was synthesized by an alternate route. Protection of **7a** with tetrahydropyran gave ethyl (*Z*)-7-*O*-benzyl-6-*O*-(tetrahydropyranyl)-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enoate (**7j**).[23] Isomerization of **7j** gave ethyl (*E*)-7-*O*-benzyl-6-*O*-(tetrahydropyranyl)-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enoate (**7k**),[7] which was deprotected to give ester **12**. Reduction of ester **12** gave (*E*)-7-*O*-benzyl-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (**13**).[18,22]



7a 12 13 (7)

Table I summarizes the results of electrophile-mediated cyclizations of **9** (eq 8) with diiodine,[24] dibromine,[25] mercuric ethanoate,[26] and benzeneselenenyl chloride[27] and the results of electrophile-mediated cyclizations of **10** (eq 9) with diiodine and with benzeneselenenyl chloride are shown in Table II.



9 (8) 10 (9)

The stereochemical assignments and ratios of isomers of the crude cyclized products were made on the basis of ^1H and ^{13}C NMR spectra.[6,28-31] It is well established for structures based on 2,3-*O*-isopropylidene-D-ribofuranose that the *O*-isopropylidene methyl groups in β epimers resonate at 25.5 ± 0.2 and 27.5 ± 0.2 ppm ($\Delta\delta$ = 1.90 ± 0.2), whereas those in α epimers appear at 24.9 ± 0.3 and 26.3 ± 0.2 ppm ($\Delta\delta$ = 1.25 ± 0.2).[29,31] In addition, the quaternary carbon of the *O*-isopropylidene group resonates at 114.5 ± 0.6 ppm for β epimers and 112.7 ± 0.6 for α epimers.[31,32] The following experiments were performed in order to test the validity of these resonances as stereochemical markers and to determine whether five-membered rings (furanosides) or six-membered rings (pyrano-

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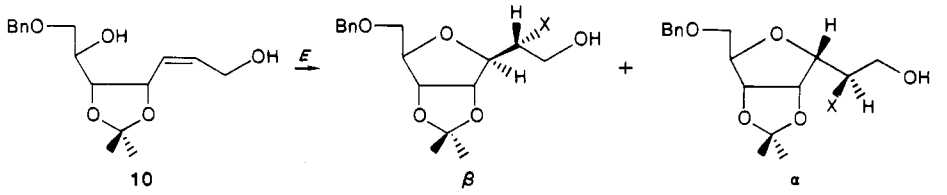
Table II. Electrophile-Mediated Intramolecular Cyclizations of (*Z*)-*O*-Benzyl-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (10)

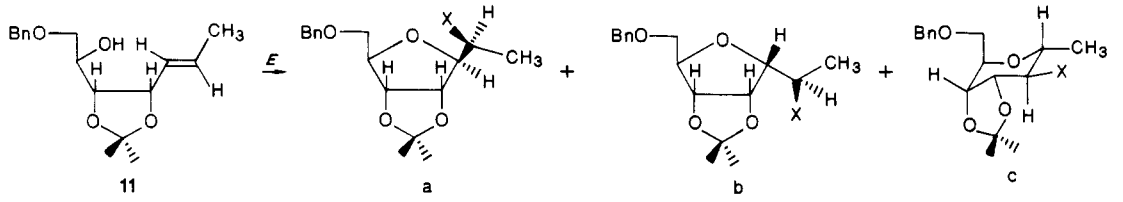


10 β α

electrophile	X	overall yield,[a] %	β	yield, %	α	yield, %
I_2	I	85	**18a**	61	**18b**	24
PhSeCl	SePh	52	**19a**	45	**19b**	7

[a] Isolated yield.

Table III. Electrophile-Mediated Intramolecular Cyclizations of (*E*)-7-*O*-Benzyl-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (11)



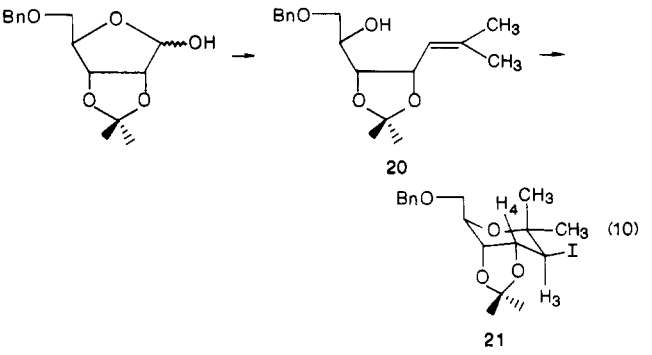
11 a b c

electrophile	X	yield,[a] %	β	yield, %	α	yield, %		yield, %
I_2	I	49	**23a**	9	**23b**	40		
NBS	Br	50	**24a**	13	**24b**	37		
$Hg(OAc)_2$	HgCl	80	**25a**	3	**25b**	58	**25c**	19[b]
PhSeCl	SePh	52	**26a**	8	**26b**	44		

[a] Isolated overall yield. [b] The stereoselectivity of this cyclization was assessed by converting the crude organomercurial products into the iodo products by treatment with diiodine and ^1H NMR integration of the three sets of methyl doublets.

sides) would be the major electrophile-mediated cyclized products from substrates **9**, **10**, **11**, and **13**.

7-*O*-Benzyl-1,2,3-trideoxy-4,5-*O*-isopropylidene-2-methyl-D-*ribo*-hept-2-enitol (**20**) was synthesized and cyclized with diiodine to the pyranoside 2,6-anhydro-7-*O*-benzyl-1,3-dideoxy-3-iodo-4,5-*O*-isopropylidene-2-*C*-methyl-D-*altro*-heptitol (**21**, eq 10) as the only isolated product. The ^1H NMR spectrum for the D-*altro*-heptitol **21** exhibited a doublet at δ 4.14 for H-3 with $J_{3,4}$ equal to 10.0 Hz, indicative of an axial–axial relationship between H-3 and H-4. The ^{13}C NMR spectrum exhibited a resonance for the quaternary carbon of the *O*-isopropylidene group at 109.79 ppm, clearly different than the resonances for a furanoside.[33] In addition, the ^{13}C NMR resonance for the ring carbon bearing the iodine was 38.92 ppm as compared to 28.46 for the ^{13}C resonance of iodine-bearing C-6 in the side chain of the furanoside 2,5-anhydro-1-*O*-benzyl-6,7-dideoxy-6-iodo-3,4-*O*-isopropylidene-D-*glycero*-L-*allo*-heptitol (**14a**). This downfield shift of C-3 in the pyran derivative is consistent with the halogen being attached to a ring rather than being part of a side chain.[34-36] A similar trend is seen with the products [2,5-anhydro-1-*O*-benzyl-6,7-dideoxy-6-bromo-3,4-*O*-isopropylidene-D-glycero-L-*allo*-heptitol (**15a**), 3,6-anhydro-7-*O*-benzyl-1,2-dideoxy-2-bromo-4,5-*O*-isopropylidene-D-glycero-D-*gluco*-heptitol (**15b**), 2,6-anhydro-7-*O*-benzyl-1,3-dideoxy-3-bromo-4,5-*O*-isopropylidene-D-*glycero*-D-*gluco*-heptitol (**15c**)] from the *N*-bromosuccinimide-mediated cyclization of **9**. Three resonances at 53.72, 49.69, and 48.31 ppm appeared in a ratio of approximately 1.5:8:0.5, corresponding to C-3 of the pyran derivative **15c**, C-2 of the L-*allo*-heptitol **15a**, and C-2 of the D-*gluco*-heptitol **15b**, respectively.



20 21 (10)

For unequivocal proof of the stereochemistry of the benzeneselenenyl chloride mediated cyclization product from **9**, 2,5-anhydro-1-*O*-benzyl-6,7-dideoxy-3,4-*O*-isopropylidene-6-*Se*-phenyl-6-seleno-D-*glycero*-L-*allo*-heptitol (**17a**) and 3,6-anhydro-7-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-2-*Se*-phenyl-2-seleno-D-*glycero*-D-*gluco*-heptitol (**17b**) were subjected to an oxidation/elimination reaction (eq 11).[37] The elimination products were separated by flash chromatography and integration of the alkene region revealed three protons. Decoupling experiments firmly established that a vinyl group was present

(32) The limits for the *O*-isopropylidene methyls for α-epimers may be too narrow. We have found *O*-isopropylidene methyl resonances for α-epimer (**23a**) at 26.66 and 25.37 ppm.

(33) The *O*-isopropylidene methyl carbons could not be unequivocally determined owing to the presence of other geminal methyl groups in the molecule.

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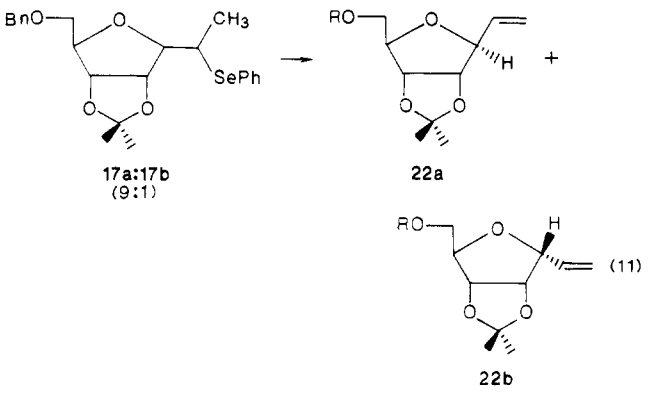
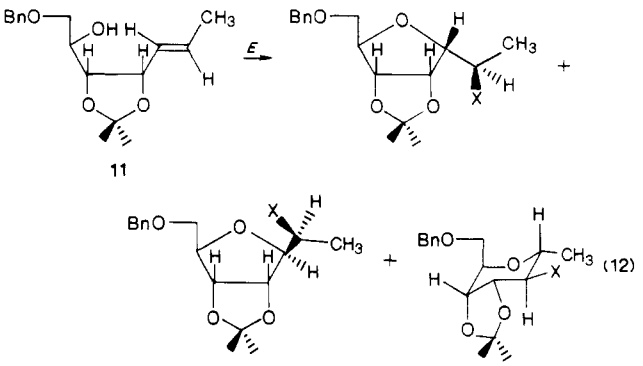


and that the quaternary carbons of the the *O*-isopropylidene carbons had resonances at 114.65 and 112.66 ppm for 3,6-anhydro-7-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-D-*allo*-hept-1-enitol (**22a**) and 3,6-anhydro-7-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-D-*altro*-hept-1-enitol (**22b**), respectively. In addition, H-5 for D-*allo*-hept-1-enitol **22a** appeared as a doublet of doublets with $J_{5,6}$ equal to 4.0 Hz while H-5 for D-*altro*-hept-1-enitol **22b** appeared as a broad doublet with $J_{5,6}$ equal to 0.8 Hz, consistent with the stereochemical assignment of the β epimer for **22a** and the α epimer for **22b**.[28,30] Thus, it appears that ^1H and ^{13}C NMR may be used to establish the structures of isomers and the regiochemistry of ring closure (i.e., five- versus six-membered) in these systems.

An examination of Tables I and II reveals that the *major product* in each cyclization is the *allo* epimer and the degree of β-selectivity is very dependent on the electrophile used. Benzeneselenenyl chloride is the most selective electrophile with both **9** and **10**. One reasonable explanation is that benzeneselenenyl chloride may be a less reactive electrophile than the others used in this study.

When diiodine is the electrophile, substitution of a hydroxymethyl for a methyl (cf. **9** and **10**) changes the regiochemistry of the ring closure and decreases the overall yield for the cyclization. When benzeneselenenyl chloride is the electrophile, the regiochemistry of the closure is not altered although the overall yield of cyclization decreases. However, in both cases, the percentage of the β (*allo*) epimer in the reaction mixture (i.e. yield of β (*allo*) epimer (%) ÷ overall yield (%) × 100) remains essentially the same (Table I, Table II). In other words, a hydroxymethyl group appears not to be any more sterically demanding than a methyl group in the cyclization transition state. In addition, a (*Z*)-methyl substituent on the alkene appears to reverse the usual selectivity observed during the electrophile-mediated cyclizations of unsubstituted terminal olefins.[1,4-6,8-10,44-49] However, in the presence of an electron-donating methyl group (i.e., carbocation stabilizing), six-membered ring formation becomes competitive. Addition of a second methyl group to the double bond (i.e., **20**) gives the pyranoside as the only isolated product (eq 10) on iodoetherification. This appears to limit the useful types of substrates for formation of functionalized β (*allo*) furanosides to either the benzeneselenenyl chloride mediated cyclization (vide supra) or the diiodine-mediated cyclization of the (*Z*)-D-*ribo*-hept-2-enoate (**7a**).[7]

In order to provide additional support that the origin of the β-selectivity was steric in nature, electrophile-mediated cyclizations of (*E*)-D-*ribo*-hept-2-enitol (**11**) were studied. The results of these cyclizations of **11** with diiodine, dibromine, mercuric acetate, and benzeneselenenyl chloride (eq 12) are summarized in Table III. These



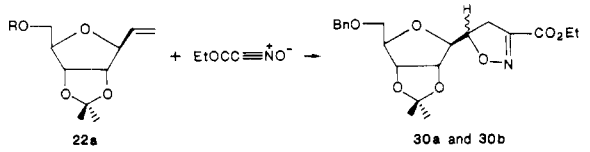
results show that with an *E* double bond, the α (*altro*) epimer (i.e., a cis relationship between H-3 and H-4) is the major five-membered ring product. Benzeneselenenyl chloride again shows the best selectivity and six-membered ring formation competes with five-membered ring formation when mercury is the electrophile.

3,6-Anhydro-7-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-2-*Se*-phenyl-2-seleno-D-*glycero*-D-*allo*-heptitol (**26a**) and 3,6-anhydro-7-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-2-*Se*-phenyl-2-seleno-D-*glycero*-D-*manno*-heptitol (**26b**) were subjected to an oxidation/elimination reaction and the resulting alkenes (74%) were separated by chromatography. The major product (**22b**, α, *altro*) was identical in all respects with the minor product isolated from the oxidation–elimination reactions of compounds **17a** and **17b** (eq 11). Thus, with this methodology it is possible to control the stereochemistry at C-3 by olefin geometry and to stereoselectivity attach a vinyl group to C-3 for further elaboration.[39]

The results of diiodine-mediated cyclization of **13** are shown in eq 13 (61% overall yield). This cyclization gave the α furanoside 3,6-anhydro-7-*O*-benzyl-2-deoxy-2-iodo-4,5-*O*-isopropylidene-D-*glycero*-D-*manno*-heptitol (**27a**) and the pyranoside 2,6-anhydro-7-*O*-benzyl-3-deoxy-3-iodo-4,5-*O*-isopropylidene-D-*glycero*-D-*manno*-heptitol (**27b**) in a ratio of 9:1 as determined by ^1H and ^{13}C NMR. None

(38) Gais, H. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 143–145.

(39) A nitrile oxide cycloaddition reaction[40] of alkene **22a** with carbethoxyformonitrile oxide (CEFNO)[41] was performed. Preliminary results suggest a 1:1 mixture of diastereomeric isoxazolines which are tentatively assigned structures **30a** and **30b**. There appears to be no facial selectivity (i.e. no "antiperplanar effect") shown by the dipole toward alkene **22a**.



(40) Kozikowski, A. P.; Ghosh, A. K. *J. Org. Chem.* **1984**, *49*, 2762–2772.

(41) Kozikowski, A. P.; Adamczyk, M. *J. Org. Chem.* **1983**, *48*, 366–370, and references cited therein.

(42) Tronchet, M. J.; Nguyen-Xuan, T. *Carbohydr. Res.* **1978**, *67*, 469–478.

(43) Lessard, J.; Saunders, J. K.; Viet, M. T. P. *Tetrahedron Lett.* **1982**, *23*, 2059–2062.

(44) Kahn, S. D.; Pau, C. F.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7396.

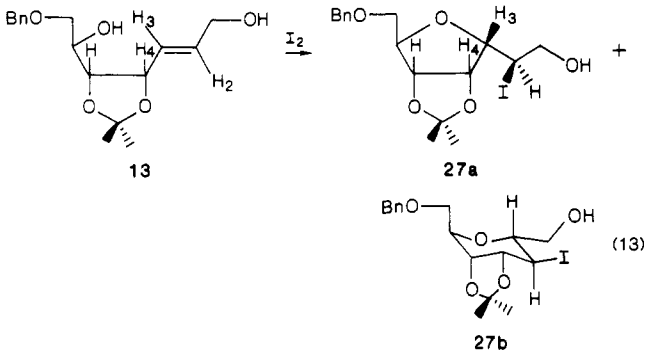
(45) Kahn, S. D.; Pau, C. F.; Chamberlin, A. R.; Hehre, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 650–663, and references cited therein.

(46) Kahn, S. D.; Hehre, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 666.

(47) Chamberlin, A. R.; Mulholland, R. L., Jr.; Kahn, S. D.; Hehre, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 672–677, and references cited therein.

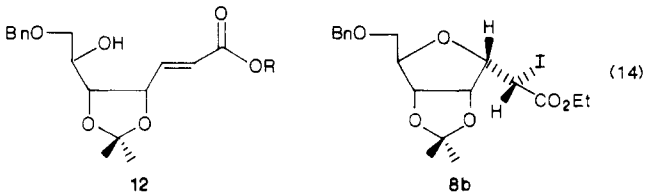
(48) Houk, K. N.; Moses, S. R.; Wu, Y.-D.; Rondan, N. G.; Jäger, V.; Schohe, R.; Fronczek, R. *J. Am. Chem. Soc.* **1984**, *106*, 3880.

(49) In Barret's system[13] there is competition between a steric component (*Z*) and an electron-withdrawing group (*E*). Apparently, the preference for the allylic ether to eclipse the prochiral olefin due to the EWG is the dominant factor leading to the modest β-selectivity observed.



of the β anomer of **27a** was obtained. The major product **27a** was previously reported as a pyran derivative.[7] As in the *Z* series, when diiodine is the electrophile, substitution of a hydroxymethyl for a methyl (cf. **11** and **13**) changes the regiochemistry of the ring closure. However, unlike the *Z* diastereomer **10**, the stereoselectivity of the diiodine-mediated cyclization of **13** increased.

Comparison of the stereochemical results of the cyclizations of **11** to those obtained from the cyclization of the (*E*)-hept-2-enoate **12** (eq 14)[7] leads to the following conclusions.



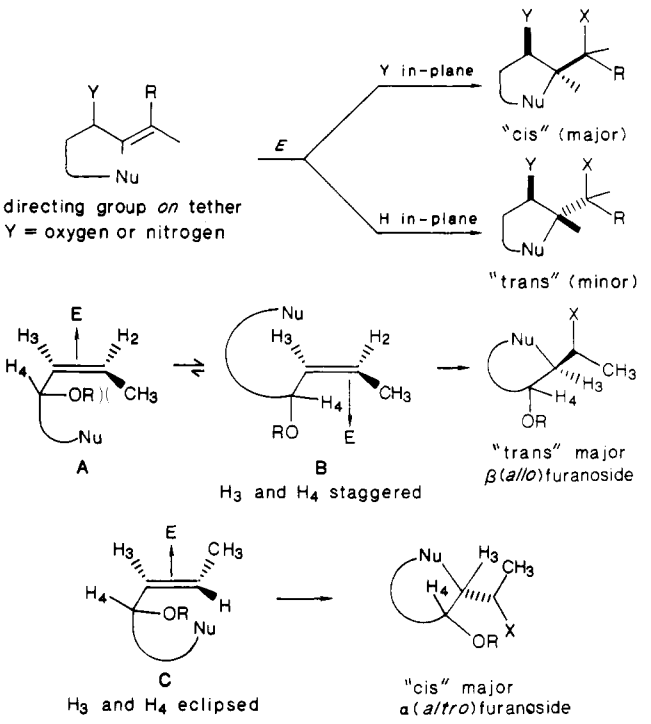
(1) For *E* olefins **11** and **12**, the stereochemical outcome of the diiodine-mediated cyclization was independent of the electronic nature of the *E* substituent. This also proved true for *E* olefins **12** and **13**. Analysis of the furanosides from the diiodine-mediated cyclization of these olefins (**12** and **13**) revealed only the presence of the α epimers (**8b** and **27a**).

(2) The stereoselectivity of the cyclization of **11** is electrophile dependent with benzeneselenenyl chloride mediated cyclization being the most stereoselective (D-*allo*-heptitol (**26a**): D-*manno*-heptitol (**26b**) = 1:5.6). The D-*manno*-heptitol (α epimer) is the major product with each electrophile (Table III).

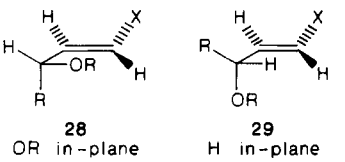
(3) For *E* olefin **11**, with an electron-donating group γ to the allylic ether oxygen, there seems to be a preference for the cyclization to occur through the conformer in which the allylic ether oxygen eclipses the prochiral olefin (H_3 and H_4 are eclipsed, Scheme I).[1,3-10] This is the same preference seen in the cyclization of **12**, with an electron-withdrawing group γ to the allylic ether oxygen (eq 14).

The stereoselectivities observed for the cyclizations of **11** are surprising since reactivity modeling calculations show only a 1.25 kJ/mol difference (relative conformational energies) between the two low energy (abundant) forms likely to exist (eq 14).[44-48] These experimental results suggest that this energy difference may be greater than this calculated value. However, the stereoselectivity of the diiodine-mediated cyclization of **12** can be rationalized on the basis of reactivity modeling calculations. In this case, where the olefin is substituted with an *E* electron-withdrawig group, calculations show a 7.5 kJ/mol difference (relative conformational energies) between the two low energy conformers **28** and **29**.[44-48] Conformer **28** is stabilized since this conformation allows the lone pair on the oxygen to be delocalized into the π-bond. Experimentally is has been shown that with an *E* electron-withdrawing group present (X = EWG), the preferred

Scheme I. Type A Cyclizations[44-47]



conformation in solution for compounds with the general formula RCH(OR)CH=CHX is one in which the alkoxy group eclipses the double bond (**28**).[7,42,43]



For a compound such as **12**, in which an internal nucleophile is incorporated into R, this conformational preference would position the internal nucleophile to trap the activated olefin in such a manner to give the α epimer. The α epimer is the only product isolated from the diiodine-mediated cyclization of **12**.[7] From the results of the cyclizations with **11** and **13**, it appears that this conformational preference may be very general and not necessarily limited to when X is an *E* electron-withdrawing group. Moreover, these experimental results are in excellent accord with stereochemical results that would be predicted by the Hehre reactivity model.[44-47] This would be considered a type A cyclization as depicted in Scheme I.

This reactivity model (scaled down to its essentials for clarity) applies to a kinetically controlled addition reaction and assumes a reactant-like (early) transition state.[44-47] The model predicts that in reactions of this type there is a preference to cyclize through the conformer in which *the OR is in the plane of the prochiral olefin* positioning the internal nucleophile to trap from below (Y *in-plane* conformation).[44-48] In this conformation the internal nucleophile is optimally positioned for antarafacial attack on the (activated) π-bond.

The electrophile approaches from the least hindered side (syn to H-4) and the internal nucleophile cyclizes onto a π-complex before it has a chance to form an "onium ion." This leads to a preferential formation of *cis*-4,5-disubstituted-furans, lactones, pyrans, piperidines, *altro* (α) substituted ribofuranoses, and *allo* (β) substituted arabinofuranoses.[1-11,13,50-52] However, with a *Z* substituent (olefins

7a, 9, and 10), there is a destabilizing steric interaction in conformer A (cf. 28) and the preferred conformer that cyclizes is the one in which the hydrogen is in the plane of the prochiral olefin (conformer B, cf. 29). This would lead to the observed β-selectivity. When the destabilizing interaction is removed (i.e. *E*-substituted olefins 11 and 13), the prediction would be that the cyclization would proceed through the reactive conformer (conformer C, cf. conformer A and 28) leading to the α furanosides (Scheme I). The stereochemical results obtained in this study and other reports support the theoretical predictions derived from this reactivity model.[1,3-13] Thus, it appears that this may be a valid model for *a priori* predicting the stereochemical outcome of cyclizations of this type.[48,49]

Conclusions

The following conclusions may be drawn from the results described in this paper.

(1) β-Selective intramolecular cyclizations can be achieved by placing *Z* substituents on a double bond.

(2) The degree of β-selectivity achieved is dependent upon the *Z* substituent on the olefin and the electrophile chosen to mediate the cyclization.

(3) Substituents that stabilize carbocations can alter the regiochemistry of trapping by the internal nucleophile.

(4) The quaternary carbon of the *O*-isopropylidene group and the carbon bonded to a halogen on a ring or on a side chain are valid stereochemical markers for differentiating α and β furanosides from pyranosides.

(5) The reactivity model of Hehre[44-47] may be used to predict the stereochemical outcome of these kinetically controlled type A intramolecular cyclizations.

Experimental Section

General Methods. Melting points were determined in open capillary tubes with a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were performed by Robertson Laboratory, Florham Park, NJ.

Optical rotations were measured with a Perkin-Elmer 241 polarimeter in an unthermostatted 10-cm glass cell at the sodium D line.

IR spectra were obtained with a Perkin-Elmer 283 spectrophotometer. Spectra were obtained for dilute solutions in CCl_4, neat films, or KBr disks.

Medium resolution mass spectra were obtained with a Finnigan 9610 GLC-CI mass spectrometer with a Nova 3 data system operating at an ionization potential of 70 or 100 eV. Chemical ionization (CI) mass spectra were obtained by using 2-methylpropane as the reactant gas. Peaks greater than ≃10% relative intensity are generally reported.

^1H and ^{13}C NMR spectra were recorded on a Bruker 250-MHz (WM-250) spectrometer with the solvent(s) noted. Chemical shifts (δ) are reported downfield from internal Me_4Si (~0.5% for Fourier transform) at δ =0.000 ppm. Apparent coupling constants (*J*) are reported in hertz (Hz). Because of the data digitization with the FT instrument, *J* values are ±0.40 Hz maximum, but normally are accurate to ±0.20 Hz. The following descriptions are used: AB q = ab quartet, br = broad, d = doublet, m = multiplet, q = quartet, s = singlet, and t = triplet.

Silica gel 60 (230–400 mesh) was used for flash column chromatography. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F-254 (0.25 mm, precoated on glass).

Solvents used for extraction and chromatography were nanograde quality or distilled. Tetrahydrofuran (THF) and ether were distilled from sodium benzophenone anion and dichloromethane was distilled from CaH_2 prior to use. *N,N*-Dimethylmethanamide (DMF) was predried over BaO, filtered, distilled under diminished pressure from CaH_2 in the dark, and stored over 4-Å sieves. Other reagents were used as supplied or purified as noted. *n*-Butyllithium in hexane (Alfa) was titrated at 24 °C in THF with (2,5-dimethoxyphenyl)methanol.

2,6-Dimethylpyridine was predried by stirring overnight under argon with aluminum trichloride (very exothermic, 5 g of $AlCl_3$ per 100 mL of 2,6-dimethylpyridine), followed by decanting into a flame-dried flask containing calcium hydride, and stirring for an additional 4–8 h. Filtration through a pad of activated basic alumina (previously heated at 175 °C for 12 h) and vacuum distillation gave 2,6-dimethylpyridine of suitable dryness.[53]

All reactions were carried out in oven- or flame-dried glassware under argon with magnetic stirring unless otherwise noted. Solutions and liquids were delivered by syringe and cannula through rubber septa or by pressure-equalizing dropping funnels where appropriate.

Ethyl (*Z*)-7-*O*-Benzyl-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enoate (7a).[11] Solid (carbethoxymethylidene)-triphenylphosphorane (4.3 g, 12.3 mmol) was added to a solution of 5-*O*-benzyl-2,3-*O*-isopropylidene-D-ribofuranose[6] (2.30 g, 8.2 mmol) in 40 mL of dry dichloromethane. The mixture was refluxed for 4 h under argon and stirred at 24–25 °C for an additional 12–60 h. The product mixture was concentrated to a viscous yellow oil, dissolved in a minimal amount of diethyl ether, and petroleum ether (30–60 °C) was added dropwise until the solution became cloudy. The resulting mixture was cooled to −10 °C for 1 h and filtered, and the filtrate was concentrated to a pale yellow syrup which was chromatographed (115 g of silica) with 3:1:1 petroleum ether/ether/dichloromethane to give 2.3 g of **7a** (80%). Although an ^1H NMR spectrum of the crude product showed a 9/1 mixture of *Z/E* isomers by integration of H-4, none of the *E* isomer was isolated after chromatography. The isolated product was essentially pure *Z* isomer (within the limits of detection of the ^1H NMR): TLC R_f 0.20 3:1:1 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3500 (br OH), 3058, 3009 (CH, Ar), 2925, 2885 (CH_3, CH_2, CH), 1730 (CO_2R), 1660 (C=C, Ar), 1380, 1370 (CMe_2), 1200, 1100–1035 (br OR), 870, 858, 732, 695 (C=C, *Z*) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–7.28 (m, 5 H, Ph), 6.27 (dd, 1 H, $J_{3,4}$ = 8.5, $J_{2,3}$ = 12.0 Hz, H-3), 5.97 (dd, 1 H, $J_{2,3}$ = 12.0, $J_{2,4}$ = 1.0 Hz, H-2), 5.68 (app t, 1 H, $J_{4,5}$ = 6.0, $J_{3,4}$ = 8.5, $J_{2,4}$ = 1.0 Hz, H-4), 4.58 (s, 2 H, OCH_2Ph), 4.34 (dd, 1 H, $J_{5,6}$ = 7.0, $J_{4,5}$ = 6.0 Hz, H-5), 4.19 (q, 2 H, *J* = 7.0 Hz, ethyl ester CH_2), 3.79 (m, 1 H, H-6), 3.68 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7,6}$ = 6.5 Hz, H-7A or H-7B), 3.58 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7,6}$ = 6.5 Hz, H-7A or H-7B), 2.95 (d, 1 H, $J_{OH,5}$ = 4.0 Hz, OH), 1.48, 1.38 (s, 6 H, Δδ = 24.76 Hz, CMe_2), 1.29 (t, 3 H, *J* = 7.0 Hz, ethyl ester CH_3); ^{13}C NMR ($CDCl_3$) 166.46 (s, C-1), 145.17 (d, C-3), 138.28 (s, C_{quat}, Ar), 128.44–127.74 (m, C_{Ar}), 122.32 (d, C-2), 109.34 (s, CMe_2), 78.76 (d, C-4), 74.33 (d, C-5), 73.53 (t, OCH_2Ph), 71.71 (t, ethyl ester CH_2), 69.56 (d, C-6), 60.83 (t, C-7), 27.98 (q, CMe_2), 25.50 (q, CMe_2), 14.25 (q, ethyl ester, CH_3); CIMS, *m/z* 351 (MH^+), 305, 293 (base), 143, 91, 71; EIMS, *m/z* 355 (M^+ − 15), 275, 229, 199, 171, 141, 125, 112, 97, 91 (base), 84.

Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.12; H, 7.49. Found: C, 64.87; H, 7.48.

Ethyl (*Z*)-7-*O*-Benzyl-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enoate (7b). Compound **7a** was protected as a *tert*-butyldimethylsilyl ether by the procedure of Corey et al.[17] This reaction was performed in dichloromethane (1 M solution of substrate) at 25 °C with a ratio of alcohol/TBDMSiOTf/2,6-dimethylpyridine of 1:1.5:2.5. The reaction was monitored by TLC (3:1:1 petroleum ether/ether/dichloromethane) and was complete after 30 min. The reaction mixture was poured onto ice–water, the layers were separated, and the aqueous phase was extracted with additional

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(51) (a) Williams, D. L. H.; Bienvenue-Goetz, E.; Dubois, J. E. *J. Chem. Soc.* **1969**, 517. (b) Staninets, V. I.; Shilov, E. A. *Russ. Chem. Rev.* **1971**, *40*, 272.

(52) (a) do Amaral, L.; Melo, S. C. *J. Org. Chem.* **1973**, *38*, 800. (b) Cambie, R. C.; Hayward, R. C.; Roberts, J. L.; Rutledge, P. S. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1864. (c) Bernett, R. G.; Doi, J. T.; Musker, W. K. *J. Org. Chem.* **1985**, *50*, 2048.

(53) Direct distillation of 2,6-dimethylpyridine from calcium hydride was problematic due to percolation of the solvent and calcium hydride even when a Vigreaux column and/or glass wool was used. For a high yield reaction it is imperative that the 2,6-dimethylpyridine be used within 2 weeks after being dried and distilled.

dichloromethane. The organic extracts were combined and washed successively with saturated ammonium chloride and saturated sodium chloride, and dried (Na_2SO_4). Evaporation of solvent under vacuum followed by chromatographic filtration through silica (20:1 packing ratio) with 3:1:1 petroleum ether/ether/dichloromethane gave a colorless oil in 80–85% yield: TLC R_f 0.70 3:1:1 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3035, 3025, 3010 (CH, Ar), 2920, 2885, 2850 (CH_3, CH_2, CH), 1710 (CO_2R), 1638 (C=C, Z), 1460, 1450 (C=C, Ar), 1370, 1360 (CMe_2) 1250–950 (br OR), 860, 830, 770, 725, 695 (C=C, Z) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.27–7.19 (m, 5 H, Ph), 6.28 (dd, 1 H, $J_{3,4}$ = 8.5, $J_{2,3}$ = 12.0 Hz, H-3), 5.82 (dd, 1 H, $J_{2,3}$ = 12.0, $J_{2,4}$ = 1.0 Hz, H-2), 5.67 (app t, 1 H, $J_{4,5}$ = 6.0, $J_{3,4}$ = 6.0, $J_{2,4}$ = 1.0 Hz, H-4), 4.42 (s, 2 H, OCH_2Ph), 4.41 (m, 1 H, H-5), 4.09 (q, 2 H, J = 7.0 Hz, ethyl ester, CH_2), 4.0 (m, 1 H, H-6), 3.48 (m, 2 H, $J_{7A,7B}$ = 8.5 Hz, H-7A, H-7B), 1.47, 1.35 (s, 6 H, $\Delta\delta$ = 28.75 Hz, CMe_2), 1.27 (t, 3 H, J = 7.0 Hz, ethyl ester CH_3), 0.88 (s, 9 H, $SiBu^t$), 0.07 (s, 3 H, $SiMe_2Bu^t$), 0.05 (s, 3 H, $SiMe_2Bu^t$); ^{13}C NMR ($CDCl_3$) 165.85 (s, C-1), 146.68 (d, C-3), 138.48 (s, C_{quat}, Ar), 128.42–120.94 (m, C_{Ar}), 120.94 (d, C-2), 108.59 (s, CMe_2), 80.38 (d, C-4), 73.44 (d, C-5), 73.25 (t, OCH_2Ph), 72.42 (t, ethyl ester, CH_2), 71.49 (d, C-6), 60.50 (t, C-7), 27.36 (q, CMe_2), 26.11 (q, $SiBu^t$), 24.82 (q, CMe_2), 18.33 (s, $SiBu^t$), 14.41 (q, ethyl ester CH_3), –4.23 (q, $Si(Me)_2Bu^t$), –4.48 (q, $Si(Me)_2Bu^t$); CIMS, m/z 407 (MH^+ – 58), 389, 257, 91 (base); EIMS, m/z 449 (M^+ – 15), 407, 349, 285, 257, 241, 211, 199, 141, 117, 112, 91 (base), 84, 73.

Anal. Calcd for $C_{25}H_{40}O_6Si$: C, 64.76; H, 8.48. Found: C, 64.64, H, 8.98.

(Z)-7-O-Benzyl-6-O-(tert-butyldimethylsilyl)-2,3-dideoxy-4,5-O-isopropylidene-D-*ribo*-hept-2-enitol (7c).[18] The Z enoate (**7b**, 2.1 g, 4.5 mmol) was dissolved in 50 mL of dry diethyl ether, cooled to 0 °C, and Dibal (7.53 mL, 1.5 M in toluene,[54] 5.0 mmol) was added dropwise over 5 min. The reaction was stirred at 0 °C for 1 h and quenched carefully at 0 °C by the addition of 2 mL of methanol. The reaction mixture was diluted to 250 mL with diethyl ether and warmed to 25 °C. The gel was transferred to a separatory funnel and the reaction flask was rinsed thoroughly with diethyl ether. The ethereal solution was washed three times with 35-mL portions of a saturated aqueous potassium–sodium tartrate solution[6] followed by saturated sodium chloride solution. The organic layer was dried (Na_2SO_4) and filtered, and solvent was evaporated under vacuum to give a clear viscous oil (**7c**, crude 100%). Flash chromatography (57.0 g silica) in 1:1:1 petroleum ether/ether/dichloromethane yielded 1.76 g (92%) of analytically pure allylic alcohol (**7c**): TLC R_f 0.20 3:1:1 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3600 (free OH), 3580–3200 (br OH), 3100, 3080, 3045 (CH, Ar), 3000, 2970, 2950, 2900, 2880 (CH_3, CH_2, CH), 1500, 1480, 1470, 1460 (C=C, Ar), 1380, 1370 (CMe_2), 1260, 1220, 1165–1000 (br OR), 840, 780, 740, 700 (C=C, Z) cm^{-1}; ^1H NMR ($CDCl_3$) 7.36–7.27 (m, 5 H, Ph), 5.83–5.78 (m, 2 H, H-2, H-3), 4.95 (app t, 1 H, H-4), 4.53 (s, 2 H, OCH_2Ph), 4.29 (m, 1 H, H-1A or H-1B), 4.22 (app t, 1 H, $J_{4,5} \simeq J_{5,6}$ = 6.0 Hz, H-5), 4.16 (m, 1 H, H-1A or H-1B), 4.05 (m, 1 H, H-6), 3.62 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 4.0 Hz, H-7A or H-7B), 3.52 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 6.0 Hz, H-7A or H-7B), 2.15 (br s, 1 H, OH), 1.44, 1.36 (s, 6 H, $\Delta\delta$ = 20.30 Hz, CMe_2), 0.87 (s, 9 H, $SiBu^t$), 0.07 (s, 6 H, $SiMe_2Bu^t$); ^{13}C NMR ($CDCl_3$) δ 138.32 (s, C_{quat} Ar), 132.99 (d, C-2 or C-3), 128.49–127.59 (m, C_{Ar} and C-2 or C-3), 108.32 (s, CMe_2), 78.76 (d, C-4), 73.39 (t, OCH_2Ph or C-7), 72.80 (t, OCH_2Ph or C-7), 72.54 (d, C-5), 70.98 (d, C-6), 58.44 (t, C-1), 27.86 (q, CMe_2), 26.09 (q, $SiBu^t$), 25.42 (q, CMe_2), 18.29 (s, $SiBu^t$), –3.90 (q, $SiMe_2Bu^t$), –4.46 (q, $SiMe_2Bu^t$); CIMS, m/z 405 (MH^+ – 18), 365 (MH^+ – 58), 347, 215 (base), 133, 91.

Anal. Calcd for $C_{23}H_{38}O_5Si$: C, 65.36; H, 9.06. Found: C, 65.16; H, 9.08.

(Z)-7-O-Benzyl-6-O-(tert-butyldimethylsilyl)-1-chloro-1,2,3-trideoxy-4,5-O-isopropylidene-D-*ribo*-hept-2-enitol (7d).[19] Allylic alcohol **7c** (azeotroped three times with benzene, 1.76 g, 4.17 mmol) and 0.61 mL (4.59 mmol) of dry 2,4,6-trimethylpyridine were treated with 354 mg (8.34 mmol) of anhydrous lithium chloride dissolved in 10 mL of *N,N*-dimethylmethanamide. The reaction mixture was cooled to 0 °C and 0.36 mL (4.59 mmol) of freshly distilled (from P_2O_5) methanesulfonyl chloride was added. The reaction was stirred at 0 °C for 2 h and quenched by being poured onto 20 mL of ice–water. Extraction with cold (0 °C) 1:1 pentane/ether (3 × 25 mL), washing with saturated cupric nitrate·$3H_2O$ (3 × 15 mL), drying (Na_2SO_4), filtration, and evaporation of solvent under vacuum gave 1.66 g (90%) of a crude yellow oil. Flash chromatography (65 g silica) in 9:1:1 petroleum ether/ether/dichloromethane gave a clear oil (**7d**) in 64% yield. The allylic chloride (**7d**) was stable to rapid chromatography (flow rate of solvent 1.5 in./min) but decomposed if stored at 25 °C for more than 2 weeks. The allylic chloride (**7d**) was usually used immediately in the next step: TLC R_f 0.60 15:1:1 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3100, 3080, 3045, 3000 (CH, Ar), 2970, 2950, 2900, 2880 (CH_3, CH_2, CH), 1500, 1480, 1470, 1460 (C=C, Ar), 1390, 1380 (CMe_2), 1260, 1225, 1150–1000 (br OR), 875, 840, 780, 740, 700 (C=C, Z) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.37–7.27 (m, 5 H, Ph), 5.83 (m, 2 H, H-2, H-3), 4.91 (app t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 6.0 Hz, H-4), 4.53 (s, 2 H, OCH_2Ph), 4.26 (app t, 1 H, $J_{4,5} \simeq J_{5,6}$ = 6.0 Hz, H-5), 4.15 (d, 2 H, $J_{1,2}$ = 7.0 Hz, H-1), 4.06 (m, 1 H, H-6), 3.59 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 4.0 Hz, H-7A or H-7B), 3.51 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 6.0 Hz, H-7A or H-7B), 1.45, 1.37 (s, 6 H, $\Delta\delta$ = 19.87 Hz, CMe_2), 0.89 (s, 9 H, $SiBu^t$), 0.09, 0.08 (s, 6 H, $SiMe_2Bu^t$); ^{13}C NMR ($CDCl_3$) δ 138.40 (s, C_{quat}, Ar), 130.67 (d, C-2 or C-3), 128.82–127.76 (m, C_{Ar} and C-2 or C-3), 108.59 (s, CMe_2), 78.89 (d, C-4), 73.45, 72.48, 72.39 (ORD shows 1 d and 2 t but base-line resolution was not possible), 70.98 (d, C-5 or C-6), 39.31 (t, C-7), 27.90 (q, CMe_2), 26.16 (q, $SiBu^t$), 25.43 (q, CMe_2), 18.37 (s, $SiBu^t$), –3.92 (q, $SiMe_2Bu^t$), –4.39 (q, $SiMe_2Bu^t$); CIMS, m/z 405 (MH^+ – ^{35}Cl), 383 (MH^+ – 58), 347, 275, 265, 257, 251, 239, 215, 199, 175, 133, 117, 107, 91 (base), 83, 71.

Anal. Calcd for $C_{23}H_{37}ClO_4Si$: C, 62.63; H, 8.45; Cl, 8.03. Found: C, 62.57; H, 8.49; Cl, 8.04.

(Z)-7-O-Benzyl-6-O-(tert-butyldimethylsilyl)-1,2,3-trideoxy-4,5-O-isopropylidene-D-*ribo*-hept-2-enitol (7e). The allylic chloride **7d** (1.17 g, 2.66 mmol) was dissolved in 30 mL of dry THF and 6.65 mL of a 1 M lithium triethylborohydride solution in tetrahydrofuran[54] (6.65 mmol, Super Hydride, Aldrich) was added dropwise over 10 min. The reaction was stirred at 25 °C for 6 h and quenched at 0 °C by cautious addition of 2 mL of water. The solvent was evaporated under vacuum and the resulting oil and lithium salts were chromatographed (45.0 g silica) in 9:1:1 petroleum ether/ether/dichloromethane to yield 1.01 g (93%) of a colorless syrup (**7e**): TLC R_f 0.74 15:1:1 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3100, 3080, 3050 (CH, Ar), 3000, 2950, 2880, (CH_3, CH_2, CH), 1500, 1480, 1470, 1460 (C=C, Ar), 1390, 1375 (CMe_2), 1255, 1220, 1200–1000 (br OR), 965, 875, 840, 780, 740, 700 (C=C, Z) cm^{-1}; ^1H NMR ($CDCl_3$) 7.36–7.28 (m, 5 H, Ph), 5.75–5.61 (m, 2 H, H-2 and H-3), 4.98 (dd, 1 H, $J_{3,4}$ = 9.0, $J_{4,5}$ = 6.0 Hz, H-4), 4.53 (s, 2 H, OCH_2Ph), 4.22 (app t, 1 H, $J_{5,6} \simeq J_{4,5}$ = 6.0 Hz, H-5), 4.02 (m, 1 H, H-6), 3.62 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ 3.0 Hz, H-7A or H-7B), 3.52 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 6.0 Hz, H-7A or H-7B), 1.71 (dd, 3 H, $J_{1,2}$ = 7.0, $J_{1,3}$ = 1.0 Hz, C=CCH_3), 1.43, 1.37 (s, 6 H, $\Delta\delta$ = 17.4 Hz, CMe_2), 0.87 (s, 9 H, $SiBu^t$), 0.08 (s, 3 H, $SiMe_2Bu^t$), 0.06 (s, 3 H, $SiMe_2Bu^t$); ^{13}C NMR ($CDCl_3$) 138.47 (s, C_{quat}, Ar) 130.14–126.94 (m, C_{Ar} and C-2, C-3), 107.95 (s, CMe_2), 78.92 (d, C-4), 73.36 (t, C-7 or OCH_2Ph), 72.80 (t, C-7 or OCH_2Ph), 72.48 (d, C-5 or C-6), 71.10 (d, C-5 or C-6), 27.90 (q, CMe_2), 26.12 (q, $SiBu^t$), 25.44 (q, CMe_2), 18.31 (s, $SiBu^t$), 13.47 (q, C-1), –3.85 (q, $SiMe_2Bu^t$), –4.54 (q, $SiMe_2Bu^t$); CIMS, m/z 349 (MH^+ – 58), 331, 265, 241, 217, 199, 173, 145, 133, 117, 109, 91 (base).

Anal. Calcd for $C_{23}H_{38}O_4Si$: C, 67.93; H, 9.41. Found: C, 68.01; H, 9.70.

Ethyl (E)-7-O-Benzyl-6-O-(tert-butyldimethylsilyl)-2,3-dideoxy-4,5-O-isopropylidene-D-*ribo*-hept-2-enoate (7f).[7,38] Freshly distilled ethanethiol (over 4 Å molecular sieves, 0.15 mL, 1.99 mmol, 30 mol %) was added to a precooled (0 °C) dry 100-mL, round-bottomed flask followed by 10 mL of dry tetrahydrofuran. The reaction flask was double septummed and 0.84 mL of 2.36 M *n*-BuLi (1.99 mmol) was added. The reaction mixture turned milky white and was stirred at 0 °C for 3 min. Dry **7b** (3.07 g, 6.62 mmol; azeotroped 3× with dry benzene) in 25 mL of dry tetrahydrofuran was added over 5 min at 0 °C. The milky white color disappeared and upon completion of the addition of **7b** the ice bath was removed and the reaction mixture was warmed to

(54) Aldrich Chemical Company.

25 °C. The reaction was stirred at 25 °C for 1.5 h, cooled to 0 °C, and quenched by the addition of 4.5 mL of 0.1 M HCl. Solvent was evaporated in the hood by blowing a slow stream of air over the reaction mixture. The crude yellow residue was dissolved in either ether or dichloromethane (75 mL) and transferred to a separatory funnel. Successive washings with water (25 mL), saturated sodium hydrogen carbonate (25 mL), and saturated sodium chloride (25 mL) followed by drying (Na_2SO_4) and removal of the solvent under vacuum gave 3.22 g (crude yield >100%) of a viscous yellow oil. Typically, the crude product was used directly but **7f** could be purified by chromatography on silica (60:1 packing ratio) in 9:1:1 petroleum ether/ether/dichloromethane to give 50–60% of pure (*E*)-hept-2-enoate **7f**: TLC R_f 0.30 9:1:1 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3100, 3080, 3040 (CH, Ar), 3000, 2970, 2950, 2920, 2870 (CH_3, CH_2, CH), 1735 (CO_2R), 1670 (C=C, ester), 1500, 1480, 1470, 1460, 1450 (C=C, Ar), 1390, 1380 (CMe_2), 1340, 1260, 1200–950 (br OR), 840, 780, 740, 700, 665 cm^{-1}; ^1H NMR ($CDCl_3$) 7.35–7.28 (m, 5 H, Ph), 7.11 (dd, 1 H, $J_{2,3}$ = 15.5, $J_{3,4}$ = 5.0 Hz, H-3), 6.07 (dd, 1 H, $J_{2,3}$ = 15.5, $J_{2,4}$ = 1.5 Hz, H-2), 4.74 (app t, 1 H, $J_{3,4}$ = 5.0 Hz, $J_{4,5}$ = 6.0 Hz, H-4), 4.52 (s, 2 H, OCH_2Ph), 4.30 (app t, 1 H, $J_{5,6}$ = $J_{4,5}$ = 6.0 Hz, H-5), 4.20 (q, ethyl ester, CH_2), 3.96 (m, 1 H, H-6), 3.64 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{6,7}$ = 3.0 Hz, H-7A or H-7B), 3.53 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{6,7}$ = 5.0 Hz, H-7A or H-7B), 1.50, 1.38 (s, 6 H, CMe_2), 1.29 (t, 3 H, J = 7.0 Hz, ethyl ester, CH_3), 0.89 (s, 9 H, $SiBu^t$), 0.11, 0.09 (s, 6 H, $SiMe_2Bu^t$); ^{13}C NMR ($CDCl_3$) 166.24 (s, C-1), 145.13 (d, C-3), 138.40 (s, C_{quat}, Ar), 128.50–127.64 (m, C_{Ar}), 122.87 (d, C-2), 109.17 (s, CMe_2), 78.62 (d, C-4), 76.86 (d, C-5), 73.54 (t, OCH_2Ph), 72.71 (t, C-7), 71.44 (d, C-6), 60.47 (t, ethyl ester, CH_2), 27.87 (q, CMe_2), 26.24 (q, $SiBu^t$), 25.58 (q, CMe_2), 18.46 (s, $SiBu^t$), 14.49 (q, ethyl ester, CH_3), –3.68 (q, $SiMe_2Bu^t$), –4.68 (q, $SiMe_2Bu^t$); CIMS, m/z 407 (MH^+ – 58), 257, 213, 147, 107, 91 (base).

Anal. Calcd for $C_{25}H_{40}SiO_5$: C, 64.64; H, 8.98. Found: C, 64.84; H, 8.87.

(*E*)-7-*O*-Benzyl-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (7g). The experimental procedures used in the *Z* series were used to make the analogous *E* isomers. Compound **7g** was obtained in 89% yield from **7f** (50% overall yield from **7b**): TLC R_f 0.3 3:1:1 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3700–3200 (br OH), 3100, 3080, 3040, (CH, Ar), 3000, 2980, 2950, 2900, 2880 (CH_3, CH_2, CH), 1500, 1470, 1460 (C=C, Ar), 1390, 1380 (CMe_2), 1260, 1220, 1200–950 (br OR), 875, 840, 780, 740, 700, 670 cm^{-1}; ^1H NMR ($CDCl_3$) 7.30–7.25 (m, 5 H, Ph), 5.82–5.79 (m, 2 H, H-2, H-3), 4.55 (app t, 1 H, H-4), 4.45 (s, 2 H, OCH_2Ph), 4.15 (app t, $J_{4,5}$ = $J_{5,6}$ = 6.5 Hz, H-5), 4.09 (br d, 2 H, H-1), 3.94 (m, 1 H, H-6), 3.58 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 3.5 Hz, H-7A or H-7B), 3.44 (dd 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 5.7 Hz, H-7A or H-7B), 1.51 (br s, 1 H, OH, D_2O exchange), 1.40, 1.30 (s, 6 H, CMe_2), 0.81 (s, 9 H, $SiBu^t$), 0.00 (s, 6 H, $SiMe_2Bu^t$); ^{13}C NMR ($CDCl_3$) 138.52 (s, C_{quat}, Ar), 133.11 (d, C-2 or C-3), 128.49–127.74 (m, C_{Ar} and C-2 or C-3), 108.47 (s, CMe_2), 78.74 (d, C-4 or C-5), 78.20 (d, C-4 or C-5), 73.53 (t, OCH_2Ph or C-1), 72.83 (t, OCH_2Ph or C-1), 71.39 (d, C-6), 63.15 (t, C-7), 27.99 (q, CMe_2), 26.23 (q, $SiBu^t$), 25.57 (q, CMe_2), 18.43 (s, $SiBu^t$), –3.67, –4.47 (q, $SiMe_2Bu^t$); CIMS, m/z 365 (MH^+ – 58), 347, 265, 257, 239, 233, 215, 197, 173, 133, 125, 117, 111, 107, 91 (base), 70.

Anal. Calcd for $C_{23}H_{38}O_5Si$: C, 65.36; H, 8.94. Found: C, 65.60; H, 8.94.

(*E*)-7-*O*-Benzyl-6-*O*-(*tert*-butyldimethylsilyl)-1-chloro-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (7h). Compound **7h** was prepared in 58% yield from **7g**. **7h**: TLC R_f 0.60 15:1:1 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3100, 3080, 3040 (CH, Ar), 3000, 2990, 2940, 2900, 2880 (CH_3, CH_2, CH), 1660 (C=C), 1500, 1480, 1470, 1460 (C=C, Ar), 1390, 1380 (CMe_2), 1260, 1220, 1200–1040 (br OR), 970, 910, 875, 840, 780, 740, 700, 665 cm^{-1}; ^1H NMR ($CDCl_3$) 7.36–7.29 (m, 5 H, Ph), 5.98 (dd, 1 H, $J_{2,3}$ = 15.5, $J_{3,4}$ = 7.0 Hz, H-3), 5.82 (dt, 1 H, $J_{2,3}$ = 15.5, $J_{1,2}$ = 6.5 Hz, H-2), 4.60 (app t, 1 H, $J_{3,4} \simeq J_{4,5}$ = 7.0 Hz, H-4), 4.52 (br s, 2 H, OCH_2Ph), 4.23 (app t, 1 H, $J_{4,5} \simeq J_{5,6}$ = 7.0 Hz, H-5), 4.05 (br d, 2 H, $J_{1,2}$ = 6.5 Hz, H-1), 4.01 (m, 1 H, H-6), 3.63 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 3.5 Hz, H-7A or H-7B), 3.51 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 5.5 Hz, H-7A or H-7B), 1.47, 1.36 (s, 6 H, CMe_2), 0.89 (s, 9 H, $SiBu^t$), 0.08 (s, 6 H, $SiMe_2Bu^t$); ^{13}C NMR ($CDCl_3$) 138.55 (s, C_{quat}, Ar), 132.08 (d, C-2 or C-3), 128.91–127.79 (m, C_{Ar} and C-2 or C-3), 108.64 (s, CMe_2), 78.73 (d, C-4 or C-5), 77.68 (d, C-4 or C-5), 73.56 (t, OCH_2Ph or C-7), 72.71 (t, $O\text{-}CH_2Ph$ or C-7), 71.33 (d, C-6), 44.42 (t, C-1), 27.99 (q, CMe_2), 26.28 (q, $SiBu^t$), 25.56 (q, CMe_2), 18.46 (s, $SiBu^t$), –3.71 (q, $SiMe_2Bu^t$), –4.39 (q, $SiMe_2Bu^t$); CIMS, m/z 407 ($MH^+ - {}^{37}Cl$), 405 ($MH^+ - {}^{35}Cl$), 385 (MH^+ – 58), 383 (MH^+ – 58), 365, 347, 275, 265, 257, 251, 239, 175, 173, 145, 133, 125, 111, 91 (base).

Anal. Calcd for $C_{23}H_{37}ClO_4 \cdot {}^1/_2H_2O$: C, 61.37; H, 8.28; Cl, 7.88. Found: C, 61.19; H, 8.41; Cl, 7.55.

(*E*)-7-*O*-Benzyl-6-*O*-(*tert*-butyldimethylsilyl)-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (7i). Compound **7i** was prepared from **7h** (90%). **7i**: TLC R_f 0.7 15:1:1 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3100, 3080, 3040 (CH, Ar), 3000, 2970, 2940, 2900, 2870 (CH_3, CH_2, CH), 1470, 1460 (C=C Ar), 1385, 1375 (CMe_2), 1260, 1220, 1190–940 (br OR), 835, 780, 735, 695 cm^{-1}; ^1H NMR ($CDCl_3$) 7.50–7.28 (m, 5 H, Ph), 5.73 (m, 1 H, H-2, collapses to a doublet with $J_{2,3}$ = 15.5 Hz upon irradiating C=CCH_3), 5.64 (dd, 1 H, $J_{2,3}$ = 15.5, $J_{3,4}$ = 7.5 Hz, H-3), 4.55 (m, 1 H, H-4), 4.53 (s, 2 H, OCH_2Ph), 4.17 (app t, 1 H, $J_{4,5} \simeq J_{5,6}$ = 6.5 Hz, H-5), 4.01 (m, 1 H, H-6), 3.67 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 3.0 Hz, H-7A or H-7B), 3.52 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 6.0 Hz, H-7A or H-7B), 1.72 (d, 3 H, $J_{1,2}$ = 5.5 Hz, C=CCH_3), 1.45, 1.35 (s, 6 H, CMe_2), 0.88 (s, 9 H, $SiBu^t$), 0.07, 0.06 (s, 6 H, $SiMe_2Bu^t$); ^{13}C NMR ($CDCl_3$) 138.73 (s, C_{quat}, Ar), 130.12 (d, C-2 or C-3), 128.48–127.68 (m, C_{Ar} and C-2 or C-3), 108.09 (s, CMe_2), 79.18 (d, C-4 or C-5), 78.77 (d, C-4 or C-5), 73.53 (t, OCH_2Ph or C-7), 73.06 (t, OCH_2Ph or C-7), 71.39 (d, C-6), 28.10 (q, CMe_2), 26.27 (q, $SiBu^t$), 25.63 (q, CMe_2), 18.46 (s, $SiBu^t$), 18.02 (q, C-1), –3.65 (q, $SiMe_2Bu^t$), –4.48 (q, $SiMe_2Bu^t$); CIMS, m/z 365 (MH^+ – 42), 349 (MH^+ – 58), 331, 265, 241, 217 (base), 199, 173, 145, 133, 117, 109, 91, 89.

Anal. Calcd for $C_{23}H_{38}O_4Si$: C, 67.93; H, 9.41. Found: C, 67.87; H, 9.42.

Ethyl (*Z*)-7-*O*-Benzyl-6-*O*-(tetrahydropyranyl)-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enoate (7j).[23] A solution of compound **7a** (1.48 g, 4.2 mmol) in 20 mL of dry dichloromethane was cooled to 0 °C and dihydropyran (1.9 mL, 21.0 mmol, 5 equiv) was added followed by a catalytic amount (7.0 mg) of *p*-toluenesulfonic acid monohydrate. The temperature was raised slowly to 25 °C over a 1.5-h period after which time all the starting material was consumed (TLC assay 3:1:1 petroleum ether/ether/dichloromethane). Removal of solvent and excess dihydropyran under vacuum gave a yellow oil which was dissolved in 50 mL of diethyl ether. This was washed once with a solution composed of 7 mL of saturated sodium hydrogen carbonate, 7 mL of saturated sodium chloride, and 14 mL of water. The aqueous layer was extracted with diethyl ether (2 × 15 mL), and the organic layer and extracts were combined, dried over anhydrous sodium sulfate, and filtered. Removal of solvent under vacuum gave 1.80 g (98%) of a yellow oil (**7j**). The crude OTHP protected *Z* enoate **7j** was used immediately in the next step without further purification: TLC R_f 0.50 3:1:1 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3100, 3040, 3030, (CH, Ar), 2980, 2940, 2860 (CH_3, CH_2, CH), 1720 (CO_2R), 1640, 1450 (C=C, Ar), 1420, 1380, 1370 (CMe_2), 1260, 1220, 1200, 1165, 1120, 1070, 1030, 980 (br OR), 930, 905, 870, 830, 810, 735, 700 cm^{-1} (no OH stretch present); ^1H NMR ($CDCl_3$) 6.24 (dd, 1 H, $J_{2,3}$ = 11.0, $J_{3,4}$ = 7.5 Hz, H-3), 5.89 (br d, 1 H, $J_{2,3}$ = 11.0 Hz, H-2), 5.71 (app t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 7.5 Hz, H-4); CIMS, m/z 377 (MH^+ – 58), 351, 305, 293 (base), 275, 247, 203, 167, 143; EIMS, m/z 419 (M^+ – 15), 243, 224, 199, 171, 141 (base), 125, 112.

Ethyl (*E*)-7-*O*-Benzyl-6-*O*-(tetrahydropyranyl)-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enoate (7k). Compound **7k** was prepared from **7j** (crude 98%) by using the isomerization procedure described for the preparation of **7f**. The crude product (**7k**) was a yellow oil whose ^1H NMR spectrum was identical with material purified by flash column chromatography: TLC R_f 0.50 in 3:1:1 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3100, 3080, 3060, 3020 (CH, Ar), 2990, 2940, 2860 (CH_3, CH_2, CH), 1725 (CO_2R), 1660, 1490, 1450, (C=C, Ar), 1380, 1370, (CMe_2), 1330–940 (br OR), 905, 870, 810, 730, 690 cm^{-1} (no OH stretch present); ^1H NMR ($CDCl_3$) 6.98 (dd, 1 H, $J_{2,3}$ = 16.0, $J_{3,4}$ = 5.0 Hz, H-3), 6.05, 6.03 (d, 1 H, $J_{2,3}$ = 16.0, $J_{2,4}$ = 1.5 Hz, H-2, two sets of peaks due to the diastereomers created by the OTHP group), 4.79 (app t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 5.0 Hz, H-4); CIMS, m/z 377 (MH^+ – 58), 351, 293, 275, 247, 229, 203, 185, 167, 157, 143 (base), 107.

(*Z*)-7-*O*-Benzyl-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (9). Compound **7e** (813.0 mg, 2.0 mmol) was dissolved in 20 mL of dry tetrahydrofuran and 6 mL of a 1 M tetrabutylammonium fluoride in tetrahydrofuran[54] (6 mmol) solution was added dropwise over 5 min. The reaction was stirred at 25 °C for 2 h, after which time the starting material was consumed (TLC assay). The reaction was quenched by the addition of 2 mL of water and the solvent was evaporated under vacuum to give a brown oil. Chromatography on silica (25 g) with 3:1:1 petroleum ether/ether/dichloromethane gave 490.0 mg (**9**, 84%) of a yellow oil: TLC R_f 0.31 3:1:1 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3700–3300 (br OH), 3100, 3080, 3045 (CH, Ar), 3000, 2950, 2940, 2880 (CH_3, CH_2, CH), 1670 (C=C, *Z*), 1500, 1460 (C=C, Ar), 1390, 1380, (CMe_2), 1320, 1200–980 (br OR), 870, 740, 700 (C=C, *Z*) cm^{-1}; ^1H NMR ($CDCl_3$) 7.35–7.26 (m, 5 H, Ph), 5.80 (m, 1 H, H-2), 5.58 (br app t, 1 H, H-3), 5.05 (dd, 1 H, $J_{3,4}$ = 9.0, $J_{4,5}$ = 6.0 Hz, H-4), 4.59 (s, 2 H, OCH_2Ph), 4.10 (dd, 1 H, $J_{4,5}$ = 6.0, $J_{5,6}$ = 8.5 Hz, H-5), 3.85 (m, 1 H, H-6), 3.72 (dd, 1 H, $J_{7A,7B}$ = 9.5, $J_{7A\text{ or }7B,6}$ = 2.5 Hz, H-7A or H-7B), 3.59 (dd, 1 H, $J_{7A,7B}$ = 9.5, $J_{7A\text{ or }7B,6}$ = 6.5 Hz, H-7A or H-7B), 2.39 (d, 1 H, $J_{6,OH}$ = 4.0 Hz, O*H*, D_2O exchange), 1.72 (dd, 3 H, $J_{1,2}$ = 6.0, $J_{1,3}$ = 1.0 Hz, C=CCH_3), 1.44, 1.37 (s, 6 H, $\Delta\delta$ = 21.8 Hz, CMe_2); ^{13}C NMR ($CDCl_3$) 138.07 (s, C_{quat}, Ar), 129.26 (d, C-2), 128.34–127.64 (m, C_{Ar} ring), 126.13 (d, C-3), 108.46 (s, CMe_2), 77.68 (d, C-4), 73.33 (t, OCH_2Ph or C-7), 73.12 (d, C-5 or C-6), 71.94 (t, OCH_2Ph or C-7), 69.07 (d, C-5 or C-6), 27.96 (q, CMe_2), 25.48 (q, CMe_2), 13.30 (q, C=CCH_3); CIMS, *m/z* 275 (MH^+ – 18), 235 (MH^+ – 58, base), 217, 209, 199, 157, 145, 131, 127, 112, 91, 85.

Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 70.0; H, 7.99.

(*Z*)-7-*O*-Benzyl-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (10).[18,22] (*Z*)-Hept-2-enoate **7a** (350 mg, 1 mmol) was dissolved in 5 mL of anhydrous diethyl ether and cooled to 0 °C, and 5 mL of a 1 M Dibal solution in hexanes[54] (5 mmol) added dropwise slowly. The reaction was stirred at 0 °C for 40 min and quenched at 0 °C by careful addition of methanol (3 mL). The reaction mixture, at 0 °C, was diluted to 25 mL with ether and sodium fluoride (168 mg, 4 equiv) and 0.3 mL of water was added. The reaction mixture was warmed to 24 °C, stirred for 20 min, and filtered. The salts were washed with chloroform and then with ethyl acetate. Removal of solvent under vacuum left a clear oil, which was further purified by flash chromatography (9 g silica) in100% ethyl acetate to yield 166 mg (54%) of an analytically pure oil (**10**): TLC R_f 0.40 diethyl ether; IR (film) ν_{max} 3600–3100 (br OH), 3080, 3020 (CH, Ar), 2920, 2880, (CH_3, CH_2, CH), 1490, 1480 (C=C, Ar), 1380, 1370 (CMe_2), 1240, 1210, 1140–960 (br OR), 865, 800 730, 690 cm^{-1}; ^1H NMR ($CDCl_3$) 7.39–7.29 (m, 5 H, Ph), 5.92 (m, 1 H, H-2), 5.63 (app t, 1 H, $J_{2,3}$ = 11.2, $J_{3,4}$ = 9.5 Hz, H-3), 5.15 (dd, 1 H, $J_{3,4}$ = 9.5, $J_{4,5}$ = 6.0 Hz, H-4), 4.57 (AB q, 2 H, $\Delta\nu_{AB}$ = 5.2, J_{AB} = 11.0 Hz, OCH_2Ph), 4.14 (dd, 1 H, $J_{4,5}$ = 6.0, $J_{5,6}$ = 9.5 Hz, H-5), 4.07 (d AB q, 2 H, $\Delta\nu_{AB}$ = 60, J_{AB} = 12.4 Hz, H-1, D_2O exchange), 3.84 (m, 1 H, H-6), 3.73 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 3.0 Hz, H-7A or H-7B), 3.58 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 6.0 Hz, H-7A or H-7B), 3.49 (br d, 1 H, O*H*, D_2O exchange), 3.41 (br s, 1 H, O*H*, D_2O exchange), 1.47, 1.36 (s, 6 H, $\Delta\delta$ = 26.5 Hz, CMe_2); ^{13}C NMR 138.17 (s, C_{quat}, Ar), 132.02 (d, C-2), 130.02 (d, C-3), 128.61–127.91 (m, C_{Ar}), 109.44 (s, CMe_2), 77.91 (d, C-4), 73.91 (d, C-5), 73.63 (t, OCH_2Ph), 71.86 (t, C-1), 68.91 (d, C-6), 58.03 (t, C-7), 28.29 (q, CMe_2), 25.80 (q, CMe_2); CIMS, *m/z* 291 (MH^+ – 18), 251 (MH^+ – 58), 233, 215, 173, 143, 133, 125, 92 (base), 83.

Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 65.98; H, 7.89.

(*E*)-7-*O*-Benzyl-1,2,3-trideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (11). Deprotection of **7i** gave **11** (92%): TLC R_f 0.31 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3700–3300 (br OH), 3100, 3080, 3040 (CH, Ar), 3000, 2940, 2880 (CH_3, CH_2, CH), 1500, 1460 (C=C, Ar), 1390, 1380 (CMe_2), 1250, 1220, 1170, 1110, 1060 (br OR), 970, 870, 735, 700 cm^{-1}; ^1H NMR ($CDCl_3$) 7.37–7.30 (m, 5 H, Ph), 5.86 (dq, 1 H, $J_{2,3}$ = 15.5, $J_{1,2}$ = 6.5 Hz, H-2), 5.63 (ddd, 1 H, $J_{2,3}$ = 15.5, $J_{3,4}$ = 7.5, $J_{1,3}$ = 1.5 Hz, H-3), 4.65 (app t, 1 H, $J_{3,4}$ = 7.5, $J_{4,5}$ = 8.5 Hz, H-4), 4.59 (s, 2 H, OCH_2Ph), 4.06 (dd, 1 H, $J_{4,5}$ = 8.5, $J_{5,6}$ = 6.0 Hz, H-5), 3.88 (m, 1 H, H-6), 3.74 (dd, 1 H, $J_{7A,7B}$ = 9.5, $J_{7A\text{ or }7B,6}$ = 2.5 Hz, H-7A or H-7B), 3.59 (dd, 1 H, $J_{7A,7B}$ = 9.5, $J_{7A\text{ or }7B,6}$ = 7.0 Hz, H-7A or 7B), 2.38 (d, 1 H, $J_{6,OH}$ = 4.0 Hz, O*H*), 1.75 (dd, 3 H, $J_{1,2}$ = 6.5, $J_{1,3}$ = 1.5 Hz, C=CCH_3), 1.45, 1.36 (s, 6 H, CMe_2); ^{13}C NMR ($CDCl_3$) 137.99 (s, C_{quat}, Ar), 130.11 (d, C-2), 128.37–127.69 (m, C_{Ar}), 126.76 (d, C-3), 108.35 (s, CMe_2), 78.70 (d, C-4 or C-5), 77.71 (d, C-4 or C-5), 73.36 (t, C-7 or OCH_2Ph), 71.95 (t, C-7 or OCH_2Ph), 68.91 (d, C-6), 27.84 (q, CMe_2), 25.39 (q, CMe_2), 17.89 (q, C-1); CIMS, *m/z* 275 (MH^+ – 18), 235 (MH^+ – 58), 217, 209, 199, 175, 157, 143, 127 (base), 112, 91.

Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.64; H, 7.99.

Ethyl (*E*)-7-*O*-Benzyl-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enoate (12).[23] The (*E*)-hept-2-enoate **7k** (697 mg, 1.61 mmol) was dissolved in 30 mL of 4:2:1 acetic acid/tetrahydrofuran/water and heated at 45 °C. Reaction was monitored by TLC and was complete in 3 h. The solvent was evaporated under vacuum (0.5 mmHg, 40 °C) and the residue was azeotroped (3 × 7 mL) with toluene to remove any remaining acetic acid. The crude product (**12**) was purified by flash chromatography (50 g of silica) in 3:1:1 petroleum ether/ether/dichloromethane to yield 340 mg (61%) of a clear oil (**12**): TLC R_f 0.20 in 3:1:1 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3600–3300 (br OH), 3100, 3070, 3040 (CH, Ar), 3000, 2940, 2920, 2880 (CH_3, CH_2, CH), 1725 (CO_2R), 1660, 1500, 1460 (C=C, Ar), 1390, 1375 (CMe_2), 1310, 1260, 1220, 1170, 1100, 1060, 1030, 970 (br OR), 915, 870, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$) 7.40–7.30 (m, 5 H, Ph), 7.11 (dd, 1 H, $J_{2,3}$ = 16.0, $J_{3,4}$ = 5.0 Hz, H-3), 6.15 (dd, 1 H, $J_{2,3}$ = 16.0, $J_{2,4}$ = 2.0 Hz, H-2), 4.86 (app t, 1 H, $J_{3,4}$ = 5.0, $J_{4,5}$ = 6.5, $J_{2,4}$ = 2.0 Hz, H-4), 4.58 (s, 2 H, OCH_2Ph), 4.21 (q, 2 H, J = 7.0 Hz, ethyl ester CH_2), 4.18 (dd, 1 H, $J_{4,5}$ = 6.5, $J_{5,6}$ = 7.0 Hz, H-5), 3.70 (br dd, 2 H, H-6 and H-7A or H-7B), 3.56 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 7.0 Hz, H-7A or H-7B), 2.51 (br s, 1 H, O*H*, D_2O exchange), 1.49, 1.38 (s, 6 H, $\Delta\delta$ = 27.1 Hz, CMe_2), 1.30 (t, 3 H, J = 7.0 Hz, ethyl ester, CH_3); ^{13}C NMR ($CDCl_3$) 166.47 (s, C-1), 143.92 (d, C-3), 138.12 (s, C_{quat}, Ar), 128.71–127.98 (m, C_{Ar}), 122.60 (d, C-2), 109.75 (s, CMe_2), 78.05 (d, C-4), 77.08 (d, C-5), 73.74 (t, OCH_2Ph), 72.09 (t, C-7), 69.15 (d, C-6), 60.6 (t, ethyl ester, CH_2), 27.9 (q, CMe_2), 25.5 (q, CMe_2), 14.4 (q, ethyl ester, CH_3); CIMS, *m/z* 351 (MH^+), 293, 275, 247, 203, 185, 143 (base), 107; EIMS, *m/z* 335 (M^+ – 15), 229, 199, 171, 142, 125, 112 (base), 107, 101.

Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48. Found: C, 64.93; H, 7.63.

(*E*)-7-*O*-Benzyl-2,3-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-2-enitol (13).[18,22] DIBAL reduction of **12** (vide supra) gave compound **13** (62%): TLC R_f 0.40 diethyl ether; IR (film) ν_{max} 3600–3100 (br OH), 3080, 3060, 3020 (CH, Ar), 2980, 2930, 2860 (CH_3, CH_2, CH), 1490, 1450 (C=C, Ar), 1380, 1370 (CMe_2), 1250, 1170, 1150–970 (br OR), 870, 735, 690 cm^{-1}; ^1H NMR ($CDCl_3$) 7.33 (s, 5 H, Ph), 5.96 (dt, 1 H, $J_{2,3}$ = 16.0, $J_{1,2}$ = 5.0 Hz, H-2), 5.81 (br dd, 1 H, $J_{2,3}$ = 16.0, $J_{3,4}$ = 7.0 Hz, H-3), 4.69 (app t, 1 H, $J_{3,4}$ = 7.0, $J_{4,5}$ = 6.0 Hz, H-4), 4.55 (s, 2 H, OCH_2Ph), 4.11 (d, 2 H, $J_{1,2}$ = 5.0 Hz, H-1), 4.05 (dd, 1 H, $J_{4,5}$ = 6.0, $J_{5,6}$ = 9.0 Hz, H-5), 3.80 (m, 1 H, H-6), 3.70 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7,6}$ = 3.0 Hz, H-7A or H-7B), 3.57 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7,6}$ = 6.0 Hz, H-7A or H-7B), 3.30 (d, 1 H, OH, D_2O exchange), 3.02 (br s, 1 H, OH, D_2O exchange), 1.43, 1.35 (s, 6 H, $\Delta\delta$ = 21.0 Hz, CMe_2); ^{13}C NMR ($CDCl_3$) 138.25 (s, C_{quat}, Ar), 132.91 (d, C-2), 128.50–127.82 (m, C_{Ar}), 126.75 (d, C-3), 108.74 (s, CMe_2), 78.06 (d, C-4 or C-5), 77.94 (d, C-4 or C-5), 73.56 (t, OCH_2Ph), 72.19 (t, C-1), 68.97 (d, C-6), 62.56 (t, C-7), 27.94 (q, CMe_2), 25.49 (q, CMe_2); CIMS, *m/z* 291 (MH^+ – 18), 251 (MH^+ – 58), 233, 215, 183, 173, 161, 143 (base), 124, 107, 91.

Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 66.15;, H, 7.62.

2,5-Anhydro-1-*O*-benzyl-6,7-dideoxy-6-iodo-3,4-*O*-isopropylidene-D-glycero-L-*allo*-heptitol (14a) and 3,6-Anhydro-7-*O*-benzyl-1,2-dideoxy-2-iodo-4,5-*O*-isopropylidene-D-*glycero*-D-*gluco*-heptitol (14b). The previously described (method A) diiodine-mediated cyclization of **9** gave a mixture of α and β furanose products that was enriched in the *allo* (β) epimer (13.5/1, β/α, 85% overall yield). The remainder of the mass was due to a pyranose product whose structure was tentatively assigned as 2,6-anhydro-7-*O*-benzyl-1,3-dideoxy-3-iodo-4,5-*O*-isopropylidene-D-*glycero*-D-*gluco*-heptitol (**14c**). The ratio of isomers **14a**:**14b**:**14c** (10.8:1:5.6) was determined by ^1H NMR integration of the three sets of resolved methyl doublets and correlation with the ^{13}C NMR spectra for the peaks due to the quaternary carbon of the *O*-isopropylidene groups in the crude

product mixture. These isomers were inseparable by conventional preparative chromatographic methods and enrichment in any of the isomers did not occur during chromatography. Resubjecting the mixture to reaction conditions did not change the ratio of isomers. Spectral data are given for the mixture unless otherwise stated; TLC R_f (**14a, 14b, 14c**) 0.55 15:1:1 petroleum ether/ether/dichloromethane; $[\alpha]^{20}_D$ (**14a, 14b, 14c**) −9.7° (*c* 1.87, $CHCl_3$); IR (**14a, 14b, 14c**, film) ν_{max} 3100, 3080, 3040 (CH, Ar), 3000, 2950, 2880 (CH_3, CH_2, CH), 1500, 1460 (C=C, Ar), 1390, 1375 (CMe_2), 1220, 1150–1000 (br OR), 810, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$, **14a**, L-*allo*): 7.37–7.29 (m, 5 H, Ph), 4.62 (s, 2 H, OCH_2Ph), 4.59–4.55 (m, 1 H, $J_{2,3}$ = 4.0, $J_{3,4}$ = 6.5 Hz, H-3), 4.27–4.17 (m, 2 H, H-2, H-6), 3.72 (app t, 1 H, $J_{5,6} \simeq J_{4,5}$ = 4.0 Hz, H-5), 3.65 (d, 2 H, $J_{1,2}$ = 4.5 Hz, H-1), 1.93 (d, $J_{6,7}$ = 7.0 Hz, CH_3), 1.55, 1.36 (s, 6 H, $\Delta\delta$ = 48.84 Hz, CMe_2); ^1H NMR ($CDCl_3$, **14b**, D-*gluco*): 2.03 (d, $J_{1,2}$ = 6.0 Hz, CH_3); ^1H NMR ($CDCl_3$, **14c**, pyran derivative): 1.97 (d, $J_{1,2}$ = 6.6 Hz, CH_3), 1.49, 1.33 (s, 6 H, $\Delta\delta$ = 40.13 Hz, CMe_2); ^{13}C NMR ($CDCl_3$, **14a**, L-*allo*): 138.25 (s, C_{quat}, Ar), 128.67–127.67 (m, C_{Ar}), 114.61 (s, CMe_2), 88.79 (d, C-2), 84.27 (d, C-3 or C-4), 83.71 (d, C-3 or C-4), 82.59 (d, C-5), 73.80 (t, OCH_2Ph), 70.59 (t, C-1), 28.46 (d, C-6), 27.67 (q, CMe_2), 25.81 (q, CMe_2), 24.49 (q, C-7); ^{13}C NMR ($CDCl_3$ **14b**, D-*gluco*): 112.68 (s, CMe_2); ^{13}C NMR ($CDCl_3$, **14c**) 138.17 (s, C_{quat}, Ar), 110.82 (s, CMe_2), 88.36 (pyran), 84.36 (pyran), 82.68 (pyran), 80.44 (pyran), 71.62 (pyran), 36.78 (d, pyran, R_2CHI), 26.52 (q, pyran, CMe_2), 25.31 (q, pyran, CMe_2), 24.57 (q, pyran, CH_3); CIMS, *m/z* (**14a, 14b, 14c**) 419 (MH^+), 293, 201, 107, 89 (base), 85, 81, 71; EIMS, *m/z* (**14a, 14b, 14c**) 291 (M^+ − 127), 233, 169, 91 (base).

Anal. Calcd for $C_{17}H_{23}IO_4$: C, 48.82; H, 5.54; I, 30.34. Found: C, 49.10; H, 5.81; I 30.60.

Compounds **14a, 14b**, and **14c** were also prepared via a mercuric acetate mediated cyclization.[1,4,6,9] Ligand exchange via a saturated aqueous KCl quench followed by treatment of the crude organomercuriochloro compounds **16a, 16b**, and **16c** with iodine in THF[6,9,26] gave **14a, 14b**, and **14c**, respectively, in a 2.4:1:1.3 ratio.

2,5-Anhydro-1-*O*-benzyl-6,7-dideoxy-6-bromo-3,4-*O*-isopropylidene-D-*glycero*-L-*allo*-heptitol (15a) and 3,6-Anhydro-7-*O*-benzyl-1,2-dideoxy-2-bromo-4,5-*O*-isopropylidene-D-*glycero*-D-*gluco*-heptitol (15b). The *N*-bromosuccinimide cyclization of **9** in DMF as described previously[9,25] gave predominantly the β epimer **15a** along with a minor amount of the α epimer **15b** (22/1, 80%). The remainder of the mass was due to a pyran derivative whose structure was tentatively assigned as 2,6-anhydro-7-*O*-benzyl-1,3-dideoxy-3-bromo-4,5-*O*-isopropylidene-D-*glycero*-D-*gluco*-heptitol (**15c**). The ratio of isomers **15a:15b:15c** was 22:1:3.7 as determined by using C_6D_6 as the ^1H NMR solvent and correlation with the ^{13}C NMR spectra ($CDCl_3$) for the peaks due to the quaternary carbon of the *O*-isopropylidene groups in the crude product mixture. These isomers were inseparable by conventional preparative chromatographic methods and enrichment in any of the isomers did not occur during chromatography. Resubjecting the mixture to reaction conditions did not change the ratio of isomers. Spectral data are given for the mixture of these products unless otherwise stated: TLC R_f (**15a, 15b, 15c**) 0.25 9:1:1 petroleum ether/ether/dichloromethane; $[\alpha]^{25}_D$ (**15a, 15b, 15c**) 0.0° (*c* 2.43, $CHCl_3$); IR (**15a, 15b, 15c**, film) ν_{max} 3100, 3080, 3040 (CH, Ar), 3000, 2980, 2950, 2920, 2880 (CH_3, CH_2, CH), 1500, 1460 (C=C, Ar), 1390, 1375 (CMe_2), 1265, 1240, 1150–1050 (br OR), 870, 800, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$, **15a**, L-*allo*): 7.40–7.28 (m, 5 H, Ph), 4.61–4.59 (s, 3 H, OCH_2Ph and H-4), 4.54 (dd, 1 H, $J_{3,4}$ = 6.5, $J_{2,3}$ = 4.0 Hz, H-5), 4.24–4.14 (m, 2 H, H-2, H-6), 4.01 (app t, 1 H, $J_{4,5} \simeq J_{5,6}$ = 4.0 Hz, H-5), 3.64 (d, 2 H, $J_{1,2}$ = 4.5 Hz, H-1), 1.73 (d, 3 H, $J_{6,7}$ = 7.0 Hz, CH_3), 1.55, 1.36 (s, 6 H, $\Delta\delta$ = 49.38 Hz, CMe_2); ^1H NMR ($CDCl_3$, **15b**, D-*gluco*): 1.77 (d, 3 H, $J_{1,2}$ = 6.5 Hz, CH_3); ^1H NMR ($CDCl_3$, **15c**, pyran derivative): 1.76 (d, 3 H, $J_{1,2}$ = 6.5 Hz, CH_3), 1.50, 1.33 (s, 6 H, $\Delta\delta$ = 42.88 Hz, CMe_2); ^1H NMR (C_6D_6, **15a**, L-*allo*): 1.49 (d, 3 H, $J_{6,7}$ = 7.0 Hz, CH_3); ^1H NMR (C_6D_6, **15b**, D-*gluco*): 1.83 (d, 3 H, $J_{1,2}$ = 6.5 Hz, CH_3); ^1H NMR (C_6D_6, **15c**, pyran derivative): 1.62 (d, 3 H, $J_{1,2}$ = 6.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$, **15a**, L-*allo*): 138.64 (s, C_{quat}, Ar), 128.67–127.70 (m, C_{Ar}), 114.55 (s, CMe_2), 88.09 (d, C-3 or C-4), 83.86 (d, C-3 or C-4), 83.36 (d, C-2 or C-5), 82.48 (d, C-2 or C-5), 73.83 (t, OCH_2Ph), 70.60 (t, C-1), 49.69 (d, C-6), 27.72 (q, CMe_2), 25.81 (q, CMe_2), 22.02 (q, C-7); ^{13}C NMR ($CDCl_3$, **15b**, D-*gluco*): 138.37 (s, *altro* C_{quat}, Ar), 112.73 (s, CMe_2), 48.31 (d, C-2), 26.54 (q, CMe_2), 25.31 (q, CMe_2); ^{13}C NMR ($CDCl_3$, **15c**, pyran derivative) 138.29 (s, C_{quat} Ar), 110.56 (s, CMe_2), 87.53 (pyran), 53.72 (d, pyran, R_2CHBr), 28.57 (q, pyran, CMe_2), 26.81 (q, pyran, CMe_2), 20.34 (q, pyran, CH_3); CIMS, *m/z* (**15a,15b,15c**) 373 (MH^+, ^{81}Br), 371 (MH^+, ^{79}Br), 281, 279, 201 (base), 91; EIMS, *m/z* (**15a,15b,15c**) 372 (M^+, ^{81}Br), 370 (M^+, ^{79}Br), 357 (M^+, ^{81}Br − 15), 355 (M^+, ^{79}Br − 15), 233, 205, 127, 91; exact mass calcd for $C_{17}H_{23}{}^{81}BrO_4$ 372.0759, found 372.0768; exact mass calcd for $C_{17}H_{23}{}^{79}BrO_4$ 370.0779, found 370.0775.

2,5-Anhydro-1-*O*-benzyl-6,7-dideoxy-3,4-*O*-isopropylidene-6-*Se*-phenyl-6-seleno-D-*glycero*-L-*allo*-heptitol (17a) and 3,6-Anhydro-7-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-6-*Se*-phenyl-6-seleno-D-*glycero*-D-*gluco*-heptitol (17b) (9:1). Compound **9** (138 mg, 0.47 mmole) was dissolved in 5.0 mL of dry THF in a round-bottomed flask and 325 mg (2.35 mmol, 5.0 equiv) of finely powdered potassium carbonate was added.[6,9,11,12,27,49,55] The reaction mixture was cooled to −78 °C and 186 mg (0.94 mmol, 2.0 equiv) of solid benzeneselenenyl chloride[54] was added. The reaction mixture was allowed to warm to 25 °C overnight, stirred at 25 °C for an additional 6 h, and filtered, and the solids were rinsed thoroughly with tetrahydrofuran. The filtrate and washings were combined and evaporated to give a viscous yellow oil (crude **17a**, and **17b**, 100%). The crude products were chromatographed (13 g of silica) with 15:1:1 petroleum ether/ether/dichloromethane to yield 154.7 mg (73%) of a yellow oil free from diphenyl diselenide. The ratio of diastereomers **17a** and **17b** was determined by the relative peak heights in the ^{13}C NMR spectra for the peaks due to the quaternary carbon of the *O*-isopropylidene groups in the crude product mixture. These diastereomers were not separated by conventional preparative chromatographic methods and enrichment in any of the diastereomers did not occur during chromatography. Resubjecting the mixture to reaction conditions did not change the ratio of diastereomers. Spectral data are given for the product mixture unless otherwise stated: TLC R_f (**17a, 17b**) 0.35 9:1:1 petroleum ether/ether/dichloromethane; $[\alpha]^{20}_D$ (**17a, 17b**) +8.4° (*c* 0.67, $CHCl_3$); IR (**17a, 17b**, film) ν_{max} 3080, 3040 (CH, Ar), 3000, 2940, 2880, (CH_3, CH_2, CH), 1960, 1885, 1815, 1720 (CH, Ar out-of-plane bending), 1590, 1500, 1480, 1460, 1395 (C=C, Ar), 1390, 1380, (CMe_2), 1260, 1220, 1170–950, (br OR), 870, 800, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$, **17a**, L-*allo*): 7.62–7.57, 7.34–7.24 (m, 10 H, Se*Ph*, OCH_2Ph), 4.65–4.50 (m, 4 H, singlet at 4.60 for OCH_2Ph, H-3, H-4), 4.11 (app q, 1 H, $J_{1,2} \simeq J_{2,3}$ = 4.5 Hz, H-2), 4.04 (app t, 1 H, $J_{5,6}$ = 7.0, $J_{4,5}$ = 5.0 Hz, H-5), 3.62 (d, 2 H, $J_{1,2}$ = 4.5 Hz, H-1), 3.44 (m, 1 H, H-6), 1.54, 1.36 (s, 6 H, $\Delta\delta$ = 45.80 Hz, CMe_2), 1.49 (d, 3 H, $J_{6,7}$ = 7.0 Hz, CH_3) [^1H NMR resonances for the CMe_2 and the CH_3 doublet of the minor epimer (α, **17b**) were not resolvable at 250 MHz.]; ^{13}C NMR ($CDCl_3$, **17a**, L-*allo*): 138.31 (s, C_{quat}, Ar, OCH_2Ph or Se*Ph*), 134.93 (s, C_{quat}, Ar, OCH_2Ph or Se*Ph*), 129.40–127.70 (m, C_{Ar}), 114.70 (s, CMe_2), 88.08 (d, C-3 or C-4), 83.53 (d, C-3 or C-4), 83.44 (d, C-2 or C-5), 82.41 (d, C-2 or C-5), 73.80 (t, OCH_2Ph), 70.51 (t, C-1), 40.07 (d, C-6), 27.74 (q, CMe_2), 25.84 (q, CMe_2), 19.10 (q, C-7); ^{13}C NMR ($CDCl_3$, **17b**, D-*gluco*): 112.35 (s, CMe_2), 26.61 (q, CMe_2), 24.96 (q, CMe_2); EIMS, *m/z* (**17a, 17b**) 448 (MH^+), 157, 91 (base); exact mass calcd for $C_{23}H_{20}O_4Se$ 448.1153, found 448.1141.

2,5-Anhydro-1-*O*-benzyl-6-deoxy-6-iodo-3,4-*O*-isopropylidene-D-*glycero*-L-*allo*-heptitol (18a) and 3,6-anhydro-7-*O*-benzyl-2-deoxy-2-iodo-4,5-*O*-isopropylidene-D-*glycero*-D-*manno*-heptitol (18b) were prepared in 61% overall yield as described above for compounds **14a** and **14b**. A small amount of each pure epimer was obtained by preparative TLC (3× elution in 9:1:1 petroleum ether/ether/dichloromethane). Resubjecting the mixture to reaction conditions did not change the ratio of diastereomers. The spectral data given are for the 60/40 mixture of diastereomers unless otherwise stated: the R_f (**18a, 18b**) 0.20 (3:1:1 petroleum ether/ether/dichloromethane); $[\alpha]^{20}_D$ (**18a, 18b**) 0° (*c* 2.94, $CHCl_3$); IR (**18a, 18b**, film) ν_{max} 3600–3200 (br OH), 3080, 3060, 3030 (CH, Ar), 2980, 2938, 2860 (CH_3, CH_2, CH), 1490, 1450 (C=C Ar), 1380, 1375 (CMe_2), 1255, 1210, 1160, 1140–990 (br OR), 970, 850, 800, 732, 690 cm^{-1}; ^1H NMR (C_6D_6, **18a, 18b**): 7.46–7.06 (m, 5 H, Ph), 4.56 (dd, 1 H, $J_{5,6}$ = 4.5, $J_{4,5}$ = 7.0 Hz, H-5), 4.44 (dd, 1 H, $J_{3,4}$ = 4.5, $J_{4,5}$ = 7.0

(55) In the absence of potassium carbonate, the yield of the desired cyclized product was low (<10%).

Hz, H-4), 4.28 (AB q, 2 H, $\Delta\nu_{AB}$ = 11.3, $J_{A,B}$ = 12.0 Hz, OCH_2Ph), 4.14 (app q, 1 H, $J_{5,6}$ = 4.5, $J_{6,7A}$ = $J_{6,7B}$ = 4.0 Hz, H-6), 3.96 (dt, 1 H, $J_{1,2}$ = 5.5, $J_{2,3}$ = 4.5 Hz, H-2), 3.85 (app t, 1 H, $J_{2,3}$ = 4.5, $J_{3,4}$ = 4.5 Hz, H-3), 3.66 (m, 2 H, H-1), 3.40 (d AB q, 2 H, $\Delta\nu_{AB}$ = 13.8, $J_{A,B}$ = 10.5, $J_{6,7}$ = 4.0 Hz, H-7A, H-7B), 2.0 (t, 1 H, $J_{OH,1}$ = 7.0 Hz, O*H*, D_2O exchange), 1.39, 1.38, 1.12, 1.11 (s, 12 H, $\Delta\delta$ = 69.1 Hz, $\Delta\delta$ = 70.0 Hz, CMe_2); ^{1}H NMR ($CDCl_3$, **18a**, L-*allo*): 7.40–7.30 (m, 5 H, Ph), 4.63 (m, 2 H, H-4 and H-3), 4.60 (AB q, 2 H, $\Delta\nu_{AB}$ = 8.9, J_{AB} = 12.0 Hz, OCH_2Ph), 4.33 (dt, 1 H, $J_{6,7}$ = 7.0, $J_{5,6}$ = 5.0 Hz, H-6), 4.18 (app q, 1 H, $J_{2,3}$ = $J_{1,2}$ = 4.0 Hz, H-2), 3.93 (m, 3 H, H-7 and H-5), 3.65 (d, 2 H, $J_{1,2}$ = 4.0 Hz, H-1), 2.67 (br t, 1 H, $J_{7,OH}$ = 7.0 Hz, O*H*), 1.55, 1.39 (s, 6 H, $\Delta\delta$ = 47.6 Hz, CMe_2); $J_{7,OH}$ ^{1}H NMR ($CDCl_3$, **18b**, D-*manno*): 7.42–7.25 (m, 5 H, Ph), 4.94 (br d, 1 H, $J_{4,5}$ = 6.5, $J_{5,6}$ = 0.8 Hz, H-5), 4.80 (dd, 1 H, $J_{4,5}$ = 6.5, $J_{3,4}$ = 3.0 Hz, H-4), 4.54 (AB q, 2 H, $\Delta\nu_{AB}$ = 8.1, J_{AB} = 12.3 Hz, OCH_2Ph), 4.40 (m, 2 H, H-2, H-3), 4.22 (app t, 1 H, $J_{6,7}$ = 4.0 Hz, H-6), 3.91 (dd, 2 H, $J_{1,OH}$ = 7.0, $J_{1,2}$ = 4.0 Hz, H-1), 3.61 (d, AB q, 2 H, $\Delta\nu_{AB}$ = 12.8, $J_{A,B}$ = 10.5, $J_{6,7}$ = 4.0 Hz, H-7), 2.35 (t, 1 H, $J_{1,OH}$ = 7.0 Hz, O*H*), 1.49, 1.33 (s, 6 H, $\Delta\delta$ = 41.7 Hz, CMe_2); ^{13}C NMR ($CDCl_3$, **18a**, **18b**): 137.94, 128.62–127.69, 114.89 (s, *allo*, CMe_2), 112.80 (s, D-*manno*, CMe_2), 85.08, 84.73, 84.33, 83.70, 82.57, 81.97, 80.64, 73.78, 73.64, 71.25, 70.08, 66.25, 65.65, 36.95, 35.38, 27.63 (q, L-*allo*, CMe_2), 26.43 (q, D-*manno*, CMe_2), 25.73 (q, L-*allo*, CMe_2), 25.10 (q, D-*manno*, CMe_2); CIMS, *m/z* (**18a**, **18b**) 435 (MH^+), 417, 327, 199, 113, 107, 91, 81, 71 (base).

Anal. Calcd for $C_{17}H_{23}IO_4$: C, 47.02; H, 5.33; I, 29.22. Found: C, 47.08; H, 5.36; I, 28.98.

2,5-Anhydro-1-*O*-benzyl-3,4-*O*-isopropylidene-6-*Se*-phenyl-6-seleno-D-*glycero*-L-*allo*-heptitol (19a) and 3,6-anhydro-7-*O*-benzyl-4,5-*O*-isopropylidene-2-*Se*-phenyl-2-seleno-D-*glycero*-D-*manno*-heptitol (19b) (5.6:1, 45% overall yield) were prepared as described above for the synthesis of compounds **17a** and **17b**. These diastereomers were inseparable by conventional preparative chromatographic methods and enrichment in any of the diastereomers did not occur during chromatography. Resubjecting the mixture to reaction conditions did not change the ratio of diastereomers. Spectral data are given for the mixture of diastereomers unless stated otherwise: TLC R_f (**19a**, **19b**) 0.10 3:1:1 petroleum ether/ether/dichloromethane; $[\alpha]^{25}_D$ (**19a**, **19b**) +30.1° (*c* 2.68, $CHCl_3$); IR (**19a**, **19b**, film) ν_{max} 3700–3200 (br OH), 3100, 3080, 3040 (CH, Ar), 3000, 2950, 2880 (CH_3, CH_2, CH), 1960, 1880, 1840, (CH, Ar out-of-plane bending), 1600, 1500, 1485, 1460, 1395 (C=C, Ar), 1390, 1380 (CMe_2), 1260, 1220, 1180–950 (br OR), 860–800, 790, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, **19a**, L-*allo*): 7.67–7.55, 7.38–7.23 (m, 10 H, Ph), 4.79 (dd, 1 H, $J_{3,4}$ = 6.0, $J_{4,5}$ = 4.8 Hz, H-4), 4.64 (dd, 1 H, $J_{3,4}$ = 6.0, $J_{2,3}$ = 4.8 Hz, H-3), 4.60 (AB q, $\Delta\nu_{AB}$ = 8.1, J_{AB} = 12.0 Hz, OCH_2Ph), 4.32 (app t, 1 H, $J_{5,6}$ = $J_{4,5}$ = 4.8 Hz, H-5), 4.12 (app q, 1 H, $J_{1,2}$ = 6.0, $J_{2,3}$ = 4.8 Hz, H-2), 3.90 (br d, 2 H, $J_{6,7}$ = 6.0 Hz, H-7, sharpens to a doublet upon addition of D_2O), 3.64 (m, 2 H, H-1), 3.49 (m, 1 H, H-6, collapses to a triplet upon irradiating H-5), 2.60 (br s, 1 H, O*H*, D_2O exchange), 1.55, 1.36 (s, 6 H, CMe_2); ^{1}H NMR ($CDCl_3$, **19b** D-*manno*): 1.53, 1.34 (s, 6 H, CMe_2); ^{13}C NMR ($CDCl_3$, **19a**, L-*allo*): 138.08 (s, C_{quat}, Ar), 135.62 (d, C_{Ar}), 134.17 (d, C_{Ar}), 129.28–127.56 (m, C_{Ar}), 114.76 (s, CMe_2), 84.70 (d, C-4), 83.62 (d, C-2 or C-3 or C-5), 83.54 (d, C-2 or C-3 or C-5), 82.06 (d, C-2 or C-3 or C-5), 73.68 (t, OCH_2Ph), 70.09 (t, C-7), 63.90 (t, C-1), 50.87 (d, C-6), 27.66 (q, CMe_2), 25.74 (q, CMe_2); ^{13}C NMR ($CDCl_3$, **19b**, D-*manno*): 112.67 (s, CMe_2), 47.93 (d, C-2), 26.43 (q, CMe_2), 25.13 (q, CMe_2); CIMS, *m/z* (**19a**, **19b**) 447 (MH^+ – 18, base), 289, 199, 159, 143, 107, 91; exact mass calcd for $C_{23}H_{28}O_5Se$ 464.1101, found 464.1121.

7-*O*-Benzyl-1,2,3-trideoxy-4,5-*O*-isopropylidene-2-methyl-D-*ribo*-hept-2-enitol (20). Isopropyltriphenylphosphonium bromide (dried overnight at 140 °C under vacuum (15 mmHg, 1.215 g, 3.15 mmol) was dissolved in 30 mL of dry toluene (from CaH_2) in a dry two-necked flask equipped with a condenser and 1.29 mL of a 2.42 M *n*-BuLi solution in hexanes (3.12 mmol) was added dropwise. The deep red ylide was heated to gentle reflux and 420 mg (1.5 mmol) of 5-*O*-benzyl-2,3-*O*-isopropylidene-D-ribofuranose[6] in 15 mL of toluene added dropwise. After completion of the addition, the reaction mixture was refluxed for 2 h after which time all the starting material was consumed (TLC assay). The reaction mixture was cooled, quenched by the addition of 5 mL of water, and the layers were separated. The organic layer was washed with 10 mL of saturated sodium chloride, separated, dried ($MgSO_4$), and filtered. Evaporation of the solvent under vacuum gave a crude yellow oil which was purified by flash column chromatography (17.0 g silica) with 3:1:1 petroleum ether/ether/dichloromethane to yield 137.0 mg (31%) of a colorless oil (**20**): TLC R_f 0.38 3:1:1 petroleum ether/ether/dichloromethane; IR (film) ν_{max} 3660–3200 (br OH), 3100, 3080, 3040 (CH, Ar), 3000, 2940, 2880 (CH_3, CH_2, CH), 1680, 1500, 1460 (C=C, Ar), 1385, 1375 (CMe_2), 1250, 1220, 1170, 1150–970 (br OR), 920, 875, 790, 740, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.37–7.26 (m, 5 H, Ph), 5.37 (br d, 1 H, $J_{2,3}$ = 6.0 Hz, H-3), 4.96 (dd, 1 H, $J_{3,4}$ = 6.0, $J_{4,5}$ = 9.5 Hz, H-4), 4.60 (s, 2 H, OCH_2Ph), 4.06 (dd, $J_{4,5}$ = 9.5, $J_{5,6}$ = 6.0 Hz, H-5), 3.88 (m, 1 H, H-6), 3.74 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 2.5 Hz, H-7A or H-7B), 3.58 (dd, 1 H, $J_{7A,7B}$ = 10.0, $J_{7A\text{ or }7B,6}$ = 6.8 Hz, H-7A or H-7B), 2.34 (d, 1 H, OH, D_2O exchange), 1.79 (s, 3 H, CH_3), 1.74 (s, 3 H, CH_3), 1.44, 1.36 (s, 6 H, CMe_2); ^{13}C NMR ($CDCl_3$) 138.40 (s, C_{quat}, Ar or C-2), 138.26 (s, C_{quat}, Ar or C-2), 128.4 6–120.44 (m, C_{Ar}), 120.44 (d, C-3), 108.32 (s, CMe_2), 77.86 (d, C-4), 74.62 (d, C-5), 73.54 (t, OCH_2Ph), 72.04 (t, C-7), 69.39 (d, C-6), 28.07, 28.16, 25.54, 18.34 (q, C-1, C-2′, CMe_2); CIMS, *m/z* 289 (MH^+ – 18), 249 (MH^+ – 58, base), 231, 189, 171, 141, 126, 107, 99, 91.

Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.68; H, 8.78.

2,6-Anhydro-7-*O*-benzyl-1,3-dideoxy-3-iodo-4,5-*O*-isopropylidene-2-*C*-methyl-D-*altro*-heptitol (21). Compound **21** was prepared in 62% yield from **20** according to the cyclization procedure (vide supra) for **14a**, **14b**, and **14c**. **21**: TLC R_f 0.41 9:1:1 petroleum ether/ether/dichloromethane; $[\alpha]^{20}_D$ –127.8° (*c* 1.41, $CHCl_3$); IR (film) ν_{max} 3100, 3080, 3040 (CH, Ar), 3000, 2940, 2880, (CH_3, CH_2, CH), 1805, 1790, 1730, 1610 (CH Ar, out-of-plane bending), 1500, 1460 (C=C, Ar), 1390, 1375 (CMe_2), 1250, 1240, 1160, 1120, 1070, 1000 (br OR), 970, 880, 865, 815, 780, 740, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.36–7.27 (m, 5 H, Ph), 4.62 (AB q, 2 H, $\Delta\nu_{AB}$ 4.5, J_{AB} = 6.5 Hz, OCH_2Ph), 4.50 (dd, 1 H, $J_{4,5}$ = 7.0, $J_{3,4}$ = 10.0 Hz, H-4), 4.21 (dd, 1 H, $J_{4,5}$ = 7.0, $J_{5,6}$ = 9.0 Hz, H-5), 4.14 (d, 1 H, $J_{3,4}$ = 10.0 Hz, H-3), 3.68 (m, 2 H, H-6, H-7A or H-7B), 3.59 (dd, 1 H, $J_{7A,7B}$ = 11.0, $J_{6,7}$ = 6.0 Hz, H-7A or H-7B), 1.50, 1.47 (s, 6 H, CH_3), 1.44, 1.36 (s, 6 H, CMe_2); ^{13}C NMR ($CDCl_3$) 138.52 (s, C_{quat}, Ar), 128.47–127.70 (m, C_{Ar}), 109.79 (s, CMe_2), 78.52 (d, C-4), 75.56 (s, C-2), 73.71 (t, OCH_2Ph), 73.66 (d, C-5 or C-6), 71.98 (d, C-5 or C-6), 71.12 (t, C-7), 38.92 (d, C-3), 30.37, 27.69, 25.76, 25.22 (q, CMe_2, C-1 and C-2′); CIMS, *m/z* 433 (MH^+), 375 (MH^+ – 58), 267, 247, 215, 157, 141, 107, 91.

Anal. Calcd for $C_{18}H_{25}O_4I$: C, 50.01; H, 5.83; I, 29.35. Found: C, 50.27; H, 5.71; I, 29.49.

3,6-Anhydro-7-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-D-*allo*-hept-1-enitol (22a) and 3,6-Anhydro-7-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-D-*altro*-hept-1-enitol (22b). Compounds **17a** and **17b** (9/1 mixture, 154.7 mg, 0.35 mmol) were dissolved in 3.5 mL of dry dichloromethane and cooled to –78 °C. Solid *m*-chloroperbenzoic acid (91.0 mg, 0.53 mmol) was added at –78 °C.[37] The reaction was stirred at –78 °C for 2.5 h, after which time the temperature was raised to –20 °C over a period of 30 min. Dry diisopropylamine (from CaH_2, 0.073 mL, 0.53 mmol) was added and the reaction mixture was allowed to warm to 25 °C. Stirring was continued at 25 °C (about 12 h) until the clear solution turned pale yellow, indicating the reaction was complete. The solvent was evaporated under vacuum and the crude yellow oil chromatographed (8.0 g silica) with 15:1:1 petroleum ether/ether/dichloromethane to effect separation from the minor D-altro epimer (**22b**, 4.0 mg) and afford 81.0 mg (79%) of pure D-*allo* epimer (**22a**): TLC R_f 0.31 9:1:1 petroleum ether/ether/dichloromethane; $[\alpha]^{22}_D$ –50.3° (*c* 1.59, $CHCl_3$); IR (film) ν_{max} 3100, 3080, 3040, (CH Ar, vinyl), 3000, 2940, 2880, (CH_3, CH_2, CH), 1500, 1460 (C=C, Ar), 1390, 1380 (CMe_2), 1250, 1220, 1160, 1150–1050 (br OR), 990, 930 (vinyl), 870, 740, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.36–7.29 (m, 5 H, Ph), 5.92 (m, 1 H, H-2, X part of ABX pattern, seven lines), 5.38 (br d, 1 H, $J_{1A,2}$ = 17.2, $J_{1A,1B}$ = $J_{1A,3}$ = 1.3 Hz, H-1A, trans to H-2), 5.21 (br d, 1 H, $J_{1B,2}$ = 10.4, $J_{1A,1B}$ = $J_{1B,3}$ = 1.3 Hz, H-1B, cis to H-2), 4.63 (dd, 1 H, $J_{4,5}$ = 6.5, $J_{5,6}$ = 4.0 Hz, H-5), 4.60 (s, 2 H, OCH_2Ph), 4.46 (dd, 1 H, $J_{4,5}$ = 6.5, $J_{3,4}$ = 4.8 Hz, H-4), 4.35 (dd, 1 H, $J_{3,4}$ = 4.8, $J_{2,3}$ = 5.0 Hz, H-3), 4.17 (app q, 1 H, $J_{5,6}$ = 4.0, $J_{6,7}$ = 4.6 Hz, H-6), 3.61 (d, 2 H, $J_{6,7}$ = 4.6 Hz, H-7), 1.57, 1.35 (s, 6 H, $\Delta\delta$ = 54.1 Hz, CMe_2); ^{13}C NMR ($CDCl_3$) 136.45 (s, C_{quat}, Ar), 128.63 (d, C-2), 128.15–127.0 (m, C_{Ar}),

117.32 (t, C-1), 114.65 (s, CMe_2), 86.01 (d, C-5 or C-4), 85.37 (d, C-5 or C-4), 83.56 (d, C-3 or C-6), 82.71 (d, C-3 or C-6), 73.85 (t, OCH_2Ph), 70.77 (t, C-7), 27.68, 25.79 (q, CMe_2); CIMS, m/z 291 (MH^+), 233 ($MH^+ - 58$), 215, 199, 173, 143, 131, 103, 91 (base), 85; EIMS, m/z 275 ($M^+ - 15$), 199, 149, 141, 107, 91 (base), 83, 69, 59; exact mass calcd for ($C_{17}H_{22}O_4 - 15$) 275.1283, found 275.1280.

3,6-Anhydro-7-*O*-benzyl-1,2-dideoxy-2-iodo-4,5-*O*-isopropylidene-D-*glycero*-D-*allo*-heptitol (23a) and 3,6-anhydro-7-*O*-benzyl-1,2-dideoxy-2-iodo-4,5-*O*-isopropylidene-D-*glycero*-D-*manno*-heptitol (23b) were prepared (**23a**:**23b** = 1:4.3) in 49% overall yield from **11** by the procedure described for the preparation of **14a**, **14b**, and **14c**, as an inseparable mixture of diastereomers. Resubjecting the mixture to reaction conditions did not change the ratio of diastereomers. Spectral data are given for the mixture unless otherwise specified: TLC R_f (**23a**, **23b**) 0.25 15:1:1 petroleum ether/ether/dichloromethane; $[\alpha]^{25}_D$ (**23a**, **23b**) −24.3° (*c* 5.8, $CHCl_3$); IR (**23a**, **23b**, film) 3100, 3080, 3040, (CH, Ar), 3000, 2950, 2900 (CH_3, CH_2, CH), 1500, 1460 (C=C, Ar), 1390, 1380 (CMe_2), 1275, 1240, 1215, 1170, 1080, 1060, 1010, 950 (br OR), 880, 850, 810, 735, 700 cm^{-1}; ^1H NMR ($CDCl_3$, **23a**, D-*allo*): 1.93 (d, 3 H, $J_{1,2}$ = 7.0 Hz, CH_3). ^1H NMR ($CDCl_3$, **23b**, D-*manno*): 7.38–7.27 (m, 5 H, Ph), 4.86 (dd, 1 H, $J_{3,4}$ = 3.0 $J_{4,5}$ = 6.0 Hz, H-4), 4.76 (br d, 1 H, $J_{4,5}$ = 6.0 Hz, H-5), 4.55 (AB q, 2 H, $\Delta\nu_{AB}$ = 12.1, J_{AB} = 12.0 Hz, OCH_2Ph), 4.24 (m, 3 H, H-2, H-3, H-6), 3.54 (dd, 2 H, $J_{7A,7B}$ = 4.0, $J_{7A\text{ or }7B,6}$ = 1.8 Hz, H-7A, H-7B), 2.03 (d, 3 H, $J_{1,2}$ = 6.0 Hz, CH_3), 1.50, 1.36 (s, 6 H, CMe_2); ^{13}C NMR ($CDCl_3$, **23b**, D-*manno*): 138.14 (s, C_{quat}, Ar), 128–127.70 (m, C_{Ar}), 112.50 (s, CMe_2), 87.59 (d, C-4), 84.24 (d, C-5), 82.97 (d, C-3 or C-6), 82.77 (d, C-3 or C-6), 73.71 (t, OCH_2Ph or C-7), 71.39 (t, OCH_2Ph or C-7), 26.66 (q, CMe_2), 25.86 (d, C-2), 25.37 (q, CMe_2), 22.46 (q, C-1); CIMS, m/z (**23a**, **23b**) 419 (MH^+), 291, 201 (base), 143, 107, 91.

Anal. Calcd for $C_{17}H_{23}IO_4$: C, 48.82; H, 5.54; I, 30.34. Found: C, 49.06; H, 5.60; I, 30.46.

Compounds **23a** and **23b** were also be prepared from **11** via a mercuric acetate mediated cyclization. Ligand exchange via a saturated aqueous KCl quench followed by treatment of the crude organomercuriochloro compounds **25a**, **25b**, and **25c** with diiodine in THF gave **23a** and **23b** in a 1:18 ratio (70% yield). The yield was determined by integration of the methyl doublets at δ 2.03 (J = 6.0 Hz) and 1.93 (J = 7.0 Hz). The remainder of the mass was accounted for by a pyran derivative which was tentatively assigned structure **23c** (2,6-anhydro-7-*O*-benzyl-1,3-dideoxy-3-iodo-4,5-*O*-isopropylidene-D-*glycero*-D-*gluco*-heptitol). This product (**23c**) exhibited a methyl doublet at 1.96 ppm (J = 6.5 Hz) in the ^1H NMR spectrum and a ^{13}C NMR resonance for the quaternary carbon of the *O*-isopropylidene at 110.78 ppm.

3,6-Anhydro-7-*O*-benzyl-2-bromo-1,2-dideoxy-4,5-*O*-isopropylidene-D-*glycero*-D-*allo*-heptitol (24a) was prepared from **11** by using the same procedure as described for the synthesis of compounds **15a**, **15b**, and **15c**. The crude mixture (80%, crude yield) was enriched in the α epimer **(3,6-anhydro-7-*O*-benzyl-2-bromo-1,2-dideoxy-4,5-*O*-isopropylidene-D-*glycero*-D-*manno*-heptitol, 24b)**. The pure D-*manno* isomer (**24b**, 50%) was obtained by chromatography on silica (100:1 packing ratio) with 15:1:1 petroleum ether/ether/dichloromethane. Resubjecting the product mixture to reaction conditions did not change the ratio of diastereomers: TLC R_f 0.25 15:1:1 petroleum ether/ether/dichloromethane; $[\alpha]^{25}_D$ −56.5° (*c* 1.7, $CHCl_3$); IR (film) ν_{max} 3100, 3080, 3040 (CH, Ar), 3000, 2950, 2890 (CH_3, CH_2, CH), 1500, 1460 (C=C, Ar), 1390, 1380 (CMe_2), 1270, 1260, 1240, 1220, 1170, 1125, 1090, 1070, 980 (br OR), 900, 885, 850, 740, 700 cm^{-1}; ^1H NMR (**24a**, **24b**, $CDCl_3$): 7.40–7.28 (m, 5 H, Ph), 4.85 (dd, 1 H, $J_{4,5}$ = 6.0, $J_{3,4}$ = 3.3 Hz, H-4), 4.78 (dd, 1 H, $J_{4,5}$ = 6.0, $J_{5,6} \simeq$ 1.0 Hz, H-5), 4.54 (AB q, 2 H, $\Delta\nu_{AB}$ = 12.3, J_{AB} = 12.2 Hz, OCH_2Ph), 4.26–4.12 (m, 3 H, H-2, H-3, H-6), 3.56 (dd, 1 H, $J_{7A,7B}$ = 9.0, $J_{7A\text{ or }7B,6}$ = 1.5 Hz, H-7A or H-7B), 3.54 (dd, 1 H, $J_{7A,7B}$ = 9.0, $J_{7A\text{ or }7B,6}$ = 2.0 Hz, H-7A or H-7B), 1.81 (d, 3 H, $J_{1,2}$ = 6.0 Hz), 1.50, 1.37 (s, 6 H, CMe_2); ^{13}C NMR (**24a**, **24b**, $CDCl_3$): 138.10 (s, C_{quat}, Ar), 128.67–127.70 (m, C_{Ar}), 112.55 (s, CMe_2), 86.63 (d, C-4), 84.07 (d, C-5), 83.06 (d, C-3 or C-6), 82.06 (d, C-3 or C-6), 73.69 (t, OCH_2Ph or C-7), 71.30 (t, OCH_2Ph or C-7), 45.06 (d, C-2), 26.60 (q, CMe_2), 25.31 (q, CMe_2), 23.55 (q, C-1); CIMS, m/z 373 (MH^+, ^{81}Br), 371 (MH^+, ^{79}Br), 201, 143, 127, 91 (base); EIMS, m/z 357 ($M^+ - 15$, ^{81}Br), 355 ($M^+ - 15$, ^{79}Br), 127, 95, 91 (base); exact mass calcd for $C_{17}H_{23}BrO_4$ 372.0759 (^{81}Br), 370.0779 (^{79}Br), found 372.0759, 370.0777.

3,6-Anhydro-7-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-2-*Se*-phenyl-2-seleno-D-*glycero*-D-*allo*-heptitol (26a) and 3,6-Anhydro-7-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-2-*Se*-2-seleno-D-*glycero*-D-*manno*-heptitol (26b). Cyclization of **11** with benzeneselenenyl chloride as described above for **17a** and **17b** gave a 1:9 inseparable mixture of diastereomers (**26a**, **26b**) in 52% yield. Resubjecting the mixture to reaction conditions did not change the ratio of diastereomers. Spectral data are given for the mixture unless otherwise stated: TLC R_f (**26a**, **26b**) 0.15 15:1:1 petroleum ether/ether/dichloromethane; $[\alpha]^{25}_D$ (**26a**, **26b**) −67.6° (*c* 5.5, $CHCl_3$); IR (**26a**, **26b**, film) ν_{max} 3080, 3040 (CH, Ar), 1500, 1480, 1460, 1390 (C=C, Ar), 1385, 1370 (CMe_2), 1260, 1170, 1120, 1070, 1050, 1020 (br OR), 900, 870, 850, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$, **26a**, D-*allo*): 1.54 (d, 3 H, $J_{1,2}$ = 7.0 Hz, *allo*, CH_3); ^1H NMR ($CDCl_3$, **26b**, D-*manno*): 7.71–7.63, 7.44–7.24 (m, 10 H, Ph), 4.98 (dd, 1 H, $J_{4,5}$ = 6.0, $J_{5,6}$ = 1.0 Hz, H-5), 4.55 (s, 2 H, OCH_2Ph), 4.26 (app t, 1 H, $J_{6,7}$ = 4.0 Hz, H-6), 4.12 (dd, 1 H, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.7 Hz, H-3), 3.58 (d, 2 H, $J_{6,7}$ = 4.0 Hz, H-7), 3.52 (dd, 1 H, $J_{2,3}$ = 10.0, $J_{1,2}$ = 7.0 Hz, H-2), 1.56 (s, 3 H, CMe_2), 1.51 (d, 3 H, $J_{1,2}$ = 7.0 Hz, CH_3), 1.39 (s, 3 H, CMe_2); ^{13}C NMR ($CDCl_3$, **26a**, D-*allo*): 114.35 (s, CMe_2), 27.66 (q, CMe_2), 25.81 (q, CMe_2), 18.84 (q, C-1); ^{13}C NMR ($CDCl_3$, **26b**, D-*manno*): 138.30 (s, C_{quat}, OCH_2Ph or SePh), 135.61 (s, C_{quat} OCH_2Ph or SePh), 129.08–127.66 (m, C_{Ar}), 112.38 (s, CMe_2), 85.91 (d, C-4), 83.42 (d, C-3 or C-5 or C-6), 83.21 (d, C-3 or C-5 or C-6), 73.66 (t, OCH_2Ph), 71.55 (t, C-7), 37.19 (d, C-2), 26.65 (q, CMe_2), 25.29 (q, CMe_2), 19.82 (q, C-1); CIMS, m/z (**26a**, **26b**) 449 (MH^+, base), 391 ($MH^+ - 58$), 283, 233, 143, 127, 91; EIMS, m/z (**26a**, **26b**) 448 (M^+), 127, 91 (base); exact mass calcd for $C_{23}H_{28}O_4Se$ 448.1153, found 448.1139.

3,6-Anhydro-7-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-D-*allo*-hept-1-enitol (22a) and 3,6-Anhydro-7-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-D-*altro*-hept-1-enitol (22b). Oxidation of **26a** and **26b** followed by elimination using the procedure previously described above for **17a** and **17b** gave a 1:9 mixture of **22a** and **22b**. Compound **22b** was separated from the minor D-*allo* isomer (**22a**) by flash chromatography on silica (60:1 packing ratio) with 9:1:1 petroleum ether/ether/dichloromethane. The major product (**22b**, *altro*) was identical with the minor product formed from the oxidation/elimination reaction of **17a** and **17b**. **22b**: TLC R_f 0.23 9:1:1 petroleum ether/ether/dichloromethane; $[\alpha]^{20}_D$ −67.0° (*c* 1.62, $CHCl_3$); IR (film) ν_{max} 3100, 3080, 3040 (CH, Ar), 3000, 2940, 2870 (CH_3, CH_2, CH), 1500, 1460 (C=C, Ar), 1390, 1380 (CMe_2), 1270, 1210, 1165, 1150–950 (br OR), 890, 855, 790, 700 cm^{-1}; ^1H NMR (**22b**, D-*altro*, $CDCl_3$) 7.64–7.26 (m, 5 H, Ph), 5.98 (m, 1 H, H-2), 5.33 (m, 2 H, H-1), 4.84 (br d, 1 H, $J_{4,5}$ = 6.0, $J_{5,6}$ = 0.8 Hz, H-5), 4.73 (app t, 1 H, $J_{4,5}$ = $J_{3,4}$ = 6.0 Hz, H-4), 4.57 (m, 1 H, H-3), 4.54 (AB q, 2 H, $\Delta\nu_{AB}$ = 15.2, J_{AB} = 12.0 Hz, OCH_2Ph), 4.25 (app t, 1 H, $J_{6,7}$ = 4.0 Hz, H-6), 3.60 (d AB q, 2 H, $\Delta\nu_{AB}$ = 14.2, J_{AB} = 9.0, $J_{6,7}$ = 4.0 Hz, H-7), 1.52, 1.35 (s, 6 H, $\Delta\delta$ = 43.15 Hz, CMe_2); ^{13}C NMR (**22b**, D-*altro*, $CDCl_3$) 138.17 (s, C_{quat}, Ar), 133.82 (d, C-2), 128.62–127.70 (m, C_{Ar}), 118.41 (t, C-1), 112.66 (s, CMe_2), 83.81 (d),[56] 83.71 (d),[56] 83.21 (d), 83.12 (d), 73.71 (t, OCH_2Ph), 71.5 (t, C-7), 26.54 (q, CMe_2), 25.28 (q, CMe_2);[56] CIMS, m/z 291 (MH^+), 233 ($MH^+ - 58$), 215, 199, 183, 173, 143, 131, 103, 91 (base); EIMS, m/z 275 ($M^+ - 15$), 199, 141, 107, 91 (base); exact mass calcd for $C_{17}H_{22}O_4$ 290.1496, found 290.1496; exact mass calcd for $C_{16}H_{19}O_4$ ($M^+ - 15$) 275.1283, found 275.1287.

3,6-Anhydro-7-*O*-benzyl-2-deoxy-2-iodo-4,5-*O*-isopropylidene-D-*glycero*-D-*manno*-heptitol (27a) and 2,6-anhydro-7-*O*-benzyl-3-deoxy-3-iodo-4,5-*O*-isopropylidene-D-*glycero*-D-*manno*-heptitol (27b) were prepared from **13** as described above for the synthesis of **18a** and **18b**. The crude cyclization product mixture (61%) showed a minor amount of pyranose product tentatively assigned as **27b**. The ratio of isomers **27a**:**27b** was 9:1. Resubjecting the mixture to reaction conditions did not change the ratio of isomers. Spectral data are given for the mixture (**27a**, **27b**) unless otherwise stated; TLC R_f (**27a**, **27b**) 0.22 3:1:1 petroleum ether/ether/dichloromethane: $[\alpha]^{24.5}_D$ (**27a**, **27b**) −19.6° (*c* 1.43, $CHCl_3$); IR (**27a**, **27b**, film) ν_{max} 3600–3300

(56) Could be any of the four ring carbons.

(br OH), 3080, 3060, 3030 (CH, Ar), 2990, 2970, 2860, (CH_3, CH_2, CH), 1490, 1450 (C=C, Ar), 1380, 1370, (CMe_2), 1270, 1230, 1210, 1160, 1110, 1070, 1020 (br OR), 880, 850, 730, 690 cm^{-1}; ^1H NMR (**27a**, $CDCl_3$) 7.42–7.29 (m, 5 H, Ph), 4.86 (dd, 1 H, $J_{4,5}$ = 6.0, $J_{3,4}$ = 3.5 Hz, H-4), 4.77 (br d, 1 H, $J_{4,5}$ = 6.0, $J_{5,6}$ = 1.0 Hz, H-5), 4.53 (AB q, 2 H, $\Delta\nu_{AB}$ = 13.4, $J_{A,B}$ = 12.0 Hz, OCH_2Ph), 4.47 (dd, 1 H, $J_{3,4}$ = 3.6, $J_{2,3}$ = 10.3 Hz, H-3, decouples to a doublet $J_{2,3}$ = 10.3 Hz, upon irradiation of H-4), 4.30 (m, 2 H, H-2, H-6), 3.96 (app t, 2 H, $J_{1,2}$ = 6.0, $J_{1,OH}$ = 6.0 Hz, H-1), 3.55 (d AB q, 2 H, $\Delta\nu_{AB}$ = 9.0, J_{AB} = 9.0, $J_{6,7}$ = 3.0 Hz, H-7), 1.51, 1.37 (s, 6 H, $\Delta\delta$ = 34.1 Hz, CMe_2); ^{13}C NMR (**27a**, $CDCl_3$) 138.02 (s, C_{quat}, Ar), 128.73–127.75 (m, C_{Ar}), 112.76 (s, CMe_2), 86.14 (d, C-4), 84.86, 82.83, 82.56, 73.82 (t, OCH_2Ph), 71.41 (t, C-1), 67.68 (t, C-7), 30.15 (d, C-2), 26.67 (q, CMe_2), 25.35 (q, CMe_2); ^{13}C NMR ($CDCl_3$, **27b**, pyran derivative) 109.03 (s, CMe_2), 36.28 (d, R_2CHI); CIMS, *m/z* (**27a**, **27b**) 435 (MH^+), 417 (MH^+ – 18, base), 327, 309, 289, 249, 233, 199, 159, 141, 131, 107, 91.

Anal. Calcd for $C_{17}H_{23}IO_5$: C, 47.02; H, 5.33; I, 29.22. Found: C, 46.81; H, 5.40; I, 28.93.

Ethyl 5-(5-*O*-Benzyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)-2-isoxazoline-3-carboxylate (30a) and Ethyl 5-(5-*O*-Benzyl-2,3-*O*-isopropylidene-α-D-ribofuranosyl)-2-isoxazoline-3-carboxylate (30b) (1:1 Syn/Anti Mixture). Ethyl chlorooximinoacetate[41] (59.2 mg, 0.39 mmol, 1.2 equiv) was added to a solution of alkene **22a** (96.0 mg, 0.33 mmol) in 1 mL of diethyl ether. The resulting mixture was stirred for 10 min at 25 °C, and a solution of sodium carbonate (41.5 mg, 0.39 mmol) in water (0.63 mL) was added dropwise from a gas-tight 1-mL syringe through a very fine needle over a period of 3.25 h. After the addition was complete, the solution was allowed to stir for an additional 12 h.[40] The solvent was evaporated and the crude solid chromatographed (5.5 g silica) with 4:1 hexane/ethyl ethanoate to yield 55.0 mg of starting material and 60.0 mg (78%) of product. The cycloaddition gave an inseparable 1:1 mixture of diastereomers (**30a**, **30b**): TLC R_f (**30a**, **30b**) 0.19 4:1 hexane/ethyl ethanoate; $[\alpha]^{20}_D$ (**30a**, **30b**) −15.6° (*c* 0.82, $CHCl_3$); IR (**30a**, **30b**, film) ν_{max} 3100, 3080, 3040 (CH, Ar), 3000, 2950, 2880 (CH_3, CH_2, CH), 1730 (CO_2R), 1600, 1590, 1500, 1460 (C=C, Ar), 1415, 1390, 1380 (CMe_2), 1260, 1220, 1190–1000 (br OR), 930 820, 750, 700 cm^{-1} [The 1:1 mixture of diastereomers was not readily apparent from the ^1H NMR except for two sets of resonances for H-5′ (d and d AB q) and two sets of resonances for the *O*-isopropylidene groups. The two sets of resonances for H-5′ were not completely resolved and the mixture of diastereomers exhibited only 1 set of resonances in $CDCl_3$ for all other protons. However, the 1:1 mixture (**30a**, **30b**) was readily apparent in the ^{13}C NMR.]; ^1H NMR (**30a**, **30b**, $CDCl_3$) 7.36–7.27 (m, 5 H, Ph), 4.93 (dt, 1 H, $J_{4,5}$ = 10, $J_{1',5}$ = 4.5 Hz, H-5), 4.65 (dd, 1 H, $J_{3',4'}$ = 3.5, $J_{2',3'}$ = 6.5 Hz, H-3′), 4.54 (AB q, 2 H, $\Delta\nu_{AB}$ = 6.1, $J_{A,B}$ = 4.5 Hz, OCH_2Ph), 4.32 (q, 2 H, ethyl ester, CH_2), 4.20 (m, 1 H, H-4′), 4.07 (app t, 1 H, $J_{2',3'}$ = 6.5, $J_{1',2'}$ = 4.0 Hz, H-2′), 4.01 (app t, 1 H, $J_{1',2'} = J_{1',5}$ = 4.0 Hz, H-1′), 3.58 (d, 2 H, $J_{4',5'}$ = 3.5 Hz, H-5′ syn or anti), 3.50 (m, 2 H, H-5′ syn or anti), 3.22 (dd, 2 H, $J_{4,5}$ = 10.0, $J_{1',5}$ = 4.0 Hz, H-4), 1.53, 1.34 (s, 6 H, $\Delta\delta$ = 48.4 Hz, CMe_2), 1.52, 1.36 (s, 6 H, $\Delta\delta$ = 41.8 Hz, CMe_2), 1.33 (t, 3 H, ethyl ester, CH_3); ^{13}C NMR (**30a**, **30b**, $CDCl_3$) 160.58, 160.52, 151.80, 138.26, 138.0, 128.59–127.80, 114.38, 114.30, 85.56, 85.18, 84.30, 84.18, 83.33, 83.16, 82.68, 82.51, 81.98, 81.75, 73.80, 73.72, 70.89, 70.66, 62.13, 35.70, 35.42, 29.82, 27.61, 27.52, 25.66, 25.61, 14.23; CIMS, *m/z* (**30a**, **30b**) 406 (MH^+, base), 247, 234, 144, 107, 91, 81, 70; EIMS, *m/z* (**30a**, **30b**) 390 (M^+ – 15), 261, 247, 91 (base); exact mass calcd for $C_{21}H_{27}NO_7$ 405.1787, found 405.1770.

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Registry No. **15b**, 115936-32-8; **15c**, 115828-29-0; **16a**, 115828-26-7; **16b**, 115936-31-7; **16c**, 115828-27-8; **17a**, 115828-30-3; **17b**, 115936-33-9; **18a**, 99409-45-7; **18b**, 99438-70-7; **19a**, 115828-31-4; **19b**, 115936-34-0; **20**, 115828-32-5; **21**, 115828-33-6; **22a**, 115828-34-7; **22b**, 115936-35-1; **23a**, 115936-36-2; **23b**, 115936-37-3; **24a**, 115936-41-9; **24b**, 115936-42-0; **25a**, 115936-38-4; **7a**, 99409-40-2; **7b**, 115828-14-3; **7c**, 115828-15-4; **7d**, 115828-16-5; **7e**, 115828-17-6; **7f**, 115828-18-7; **7g**, 115828-19-8; **7h**, 115828-20-1; **7i**, 115857-82-4; **7j**, 115828-21-2; **7k**, 115828-22-3; **9**, 115828-23-4; **10**, 99409-44-6; **11**, 115889-74-2; **12**, 99409-42-4; **13**, 99438-69-4; **14a**, 115828-24-5; **14b**, 115936-30-6; **14c**, 115828-25-6; **15a**, 115828-28-9; **25b**, 115936-39-5; **25c**, 115936-40-8; **26a**, 115936-43-1; **26b**, 115936-44-2; **27a**, 99438-70-7; **27b**, 115936-45-3; **30a**, 115828-35-8; **30b**, 115828-36-9; (carbethoxymethylidene)triphenylphosphorane, 1099-45-2; 5-*O*-benzyl-2,3-*O*-isopropylidene-D-ribofuranose, 115857-81-3; isopropyltriphenylphosphonium bromide, 1530-33-2; ethyl chlorooximinoacetate, 14337-43-0.