An Efficient Synthesis of Anhydroalditols and Allyl C-Glycosides[1]

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Efforts to expedite production of anhydroalditols have led to a new, efficient synthesis of these compounds from alkyl glycosides. Silylation of the glycoside followed by reductive cleavage in the presence of triethylsilane and trimethylsilyl trifluoromethanesulfonate were carried out in the same reaction flask. Subsequent aqueous workup gave excellent yields of anhydroalditol(s). In some cases ring contraction was observed, but the use of bulkier silyl protecting groups gave greater yields of the expected product. This method was also shown to be an efficient means to prepare allyl C-glycosides, without any independent protecting or activating step, by simply replacing triethylsilane with allyltrimethylsilane in the synthetic scheme.

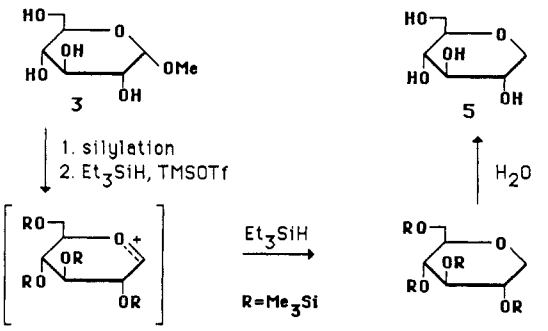
Introduction

Efforts to simplify the structural characterization of complex carbohydrates have led to the development of a new technique for carrying out "methylation analysis", namely, the reductive-cleavage method.[2-6] In prior applications of this method to the analysis of fully methylated polysaccharides, partially methylated anhydroalditols were routinely produced from the constituent monosaccharides.[3-6] In order to identify these fragments, the independent synthesis of these compounds was necessary. A variety of procedures for the preparation of anhydroalditols have been developed including catalytic hydrogenation of glycals[7] and thioglycosides,[8] nitrous acid deamination of 2-amino-2-deoxyaldoses,[9] acid-catalyzed dehydration of acylic alditols,[10] and reduction of glycosyl halides.[11-13] Unfortunately, these methods require the laborious synthesis of an appropriate fully protected intermediate or a tedious and inefficient separation of isomeric products.

The high yields produced by reductive cleavage of glycosides and the stability of alkyl ethers to reaction conditions suggested that reductive cleavage could serve as a routine method for producing anhydroalditols. Prior work from this laboratory has shown that reductive cleavage is indeed capable of producing anhydroalditols;[2] however, the need for separate protection (benzylation) and deprotection steps left this synthetic method as laborious as earlier methods.

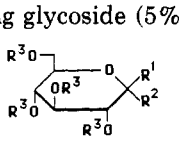
Since reductive cleavage is relatively easy to carry out, a different protection/deprotection scheme was envisioned based on silylation, which would require fewer reactions. In this report we describe an easy, efficient synthesis of a variety of anhydroalditols starting from readily obtainable alkyl glycosides. Silylation and reductive cleavage were also performed on free aldoses and disaccharides in order to determine whether anhydroalditols could be obtained from these ubiquitous materials without any prior protecting steps. The method has been extended to the production of allyl C-glycosides by replacing triethylsilane with allyltrimethylsilane as an alkylating agent. Excellent yields of the appropriate allyl C-glycosides were obtained from the methyl glycosides of glucose, ribose, and fructose.

Scheme I



Results

Reductive Cleavage of Methyl Per-O-(trimethylsilyl)-D-glucopyranosides. Methyl 2,3,4,6-tetra-O-(trimethylsilyl)-α-D-glucopyranoside (1) and its corresponding β-anomer, methyl 2,3,4,6-tetra-O-(trimethylsilyl)-β-D-glucopyranoside (2), prepared from methyl α-D-glucopyranoside (3) and methyl β-D-glucopyranoside (4), respectively, were separately treated with 5 equiv (per equiv of glycoside) of triethylsilane and 5 equiv of trimethylsilyl trifluoromethanesulfonate (TMSOTf) overnight at room temperature. The reaction was worked up by pouring it into water with thorough stirring (performed in an adequately ventilated hood). Slow addition of mixed-bed exchange resin to the stirred aqueous solution until all acid was removed (as indicated by the resin), followed by filtration and thorough evaporation of the aqueous filtrate under vacuum left a hard syrup which crystallized after a short time. Acetylation of the product and analysis by GLC (method a) demonstrated that 1,5-anhydro-D-glucitol (5) was formed in 92% yield. The remainder of the "product" consisted of 1,4-anhydro-D-glucitol (6, 3%) and starting glycoside (5%).



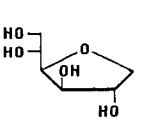
1 R^1 = H, R^2 = OMe, R^3 = $SiMe_3$

2 R^1 = OMe, R^2 = H, R^3 = $SiMe_3$

3 R^1 = R^3 = H, R^2 = OMe

4 R^2 = R^3 = H, R^1 = OMe

5 R^1 = R^2 = R^3 = H



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Sequential Silylation and Reductive Cleavage of Alkyl Glycosides. The production of 1,5-anhydro-D-glucitol (5) was simplified by performing silylation and reductive cleavage in the same flask (Scheme I), thus

(1) This investigation was supported by Grant GM34710 awarded by the Department of Health, Education, and Welfare.

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Table I. Direct Conversion of Glycosides to Anhydroalditols with Retention of Ring Size by Sequential Silylation and Reductive Cleavage

starting material	major product(s)	yield,[a] %
methyl α-D-mannopyranoside (7)	1,5-anhydro-D-mannitol (8)	97
methyl α-D-galactopyranoside (9a)	1,5-anhydro-D-galactitol (10)	97
methyl β-D-galactopyranoside (9b)	1,5-anhydro-D-galactitol (10)	100
methyl α,β-D-ribofuranoside (11a,b)	1,4-anhydro-D-ribitol (12)	98
methyl α-L-arabinofuranoside (13a)	1,4-anhydro-L-arabinitol (14)	94
methyl β-L-arabinofuranoside (13b)	1,4-anhydro-L-arabinitol (14)	97
methyl α-D-fructofuranoside (15a)	2,5-anhydro-D-mannitol (16)	81
	2,5-anhydro-D-glucitol (17)	19
methyl β-D-fructofuranoside (15b)	2,5-anhydro-D-mannitol (16)	78
	2,5-anhydro-D-glucitol (17)	19
	1,5-anhydro-D-mannitol (8)	3

[a] Analysis performed on the peracetylated derivatives by GLC.

Table II. Direct Conversion of Glycosides to Anhydroalditols (with Ring Contraction) by Sequential Silylation and Reductive Cleavage

starting material	major products	yield,[a] %
methyl β-D-arabino-pyranoside (18)	1,4-anhydro-D-arabinitol (19)[b]	95
	1,5-anhydro-D-arabinitol (20)	5
benzyl β-D-arabino-pyranoside (21)	1,4-anhydro-D-arabinitol (19)	95
	1,5-anhydro-D-arabinitol (20)	5
methyl β-D-fructo-pyranoside (22)	1,5-anhydro-D-mannitol (8)	68
	2,5-anhydro-D-mannitol (16)	28
	2,5-anhydro-D-glucitol (17)	4
methyl α-D-gluco-septanoside (23)	1,4-anhydro-D-glucitol (6)[c]	72
	1,5-anhydro-D-glucitol (5)	9
	methyl α-D-glucopyranoside (3)	19

[a] Analysis performed on the peracetylated derivatives by GLC. [b] 19 = optical isomer of 14. [c] None of the expected 1,6-anhydro-D-glucitol was observed.

eliminating the independent synthesis and isolation of the protected glucoside. Silylation was accomplished by using either BSA [bis(trimethylsilyl)acetamide] or BSTFA [bis(trimethylsilyl)trifluoroacetamide], but a higher yield of product **5** was obtained with BSTFA as the silylating reagent (93% vs. 18%), although both reagents appeared to accomplish complete silylation. In both reactions a small amount (1–3%) of **6** was formed and the remainder of the product consisted of starting material.

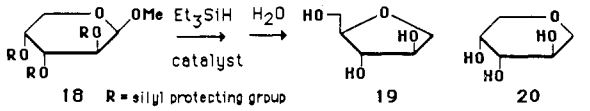
In order to explore the generality of sequential silylation and reductive cleavage, selected alkyl glycosides were silylated with BSTFA (1.5 equiv per hydroxyl group) and reductively cleaved by the addition of 5 equiv each of triethylsilane and TMSOTf. After aqueous workup, the products were analyzed as their acetyl derivatives by GLC. Reactions where little if any ring rearrangement was observed (pyranosides gave 1,5-anhydroalditols and furanosides gave 1,4- or 2,5-anhydroalditols, as appropriate) are listed in Table I, whereas in Table II are listed those reactions in which a substantial amount of ring contraction was observed. Note that 1,5-anhydro-D-mannitol (**8**) was formed as the major product from silylation and reductive

Table III. Effect of Protecting Group and Catalyst on the Amount of Ring Contraction Occurring during Silylation and Reductive Cleavage of Methyl β-D-Arabinopyranoside (18)

catalyst	protecting group	products (%)[a] 19 (furan)	20 (pyran)
Me_3SiOTf	Me_3Si	95	5
Me_3SiOTf	Et_3Si	35	65
Me_3SiOTf	t-$BuMe_2Si$	25	75
Me_3SiOTf	$ClCH_2Me_2Si$	17	83
Et_3SiOTf	Me_3Si	77	23
Et_3SiOTf	Et_3Si	26	74

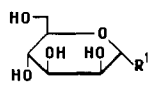
[a] Analysis performed on the peracetylated derivatives by GLC, methods b or c.

Scheme II

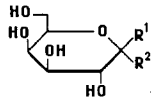


18 19 20

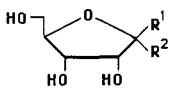
cleavage of both methyl α-D-mannopyranoside (**7**) and methyl β-D-fructopyranoside (**22**). In these reactions, however, hydride addition has taken place at two different sites, i.e., carbon 1 of the product anhydroalditol in the reduction of **7** and carbon 5 in the product from **22**. 1,5-Anhydro-L-gulitol was not detected as a product in the reduction of **22**, however, demonstrating that hydride addition to the intermediate pyran oxonium ion was stereospecific.



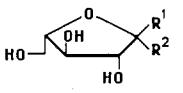
7 R^1 = OMe
8 R^1 = H



9a R^1 = H, R^2 = OMe
9b R^1 = OMe, R^2 = H
10 R^1 = R^2 = H

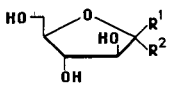


11a,b R^1, R^2 = H, OMe
12 R^1 = R^2 = H

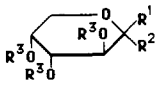


13a R^1 = OMe, R^2 = H
13b R^1 = H, R^2 = OMe
14 R^1 = R^2 = H

In an attempt to eliminate ring contraction during sequential silylation and reductive cleavage, a series of studies were performed by using methyl β-D-arabinopyranoside (**18**) as starting material and bulkier silyl protecting groups and catalysts (Table III). Less contraction occurred with bulkier and more electrophilic protecting groups or catalysts (Table III). Less ring contraction (6%) also occurred in the reductive cleavage of methyl β-D-fructopyranoside (**22**) when the bulkier triethylsilyl protecting group was used instead of the trimethylsilyl protecting group (32%, Table II).

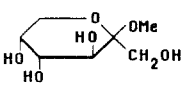


15a R^1 = CH_2OH, R^2 = OMe
15b R^1 = OMe, R^2 = CH_2OH
16 R^1 = H, R^2 = CH_2OH
17 R^1 = CH_2OH, R^2 = H



18 R^2 = R^3 = H, R^1 = OMe
20 R^1 = R^2 = R^3 = H
21 R^2 = R^3 = H, R^1 = OBn
24 R^1 = OMe, R^2 = H, R^3 = Me
25 R^1 = R^2 = H, R^3 = Me

Ring rearrangement was prevented when the hydroxyl positions were alkylated as in the reductive cleavage of



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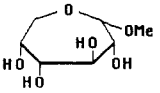

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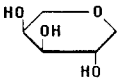

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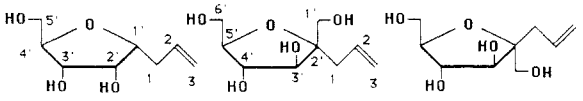
methyl 2,3,4-tri-*O*-methyl-β-D-arabinopyranoside (**24**); only the expected pyran product [1,5-anhydro-2,3,4-tri-*O*-methyl-D-arabinitol (**25**)] was formed.

Sequential Silylation and Reductive Cleavage of Selected Aldoses and Disaccharides. Silylation and reductive cleavage was also attempted with free aldoses and nonreducing disaccharides, and the results are given in Table IV. Effective reduction of glucose occurred only at elevated temperature (80 °C) and, at room temperature, only the fructofuranosyl moiety of sucrose underwent significant reduction.

***C*-Glycoside Synthesis.** In an effort to explore the reactivity of nucleophiles other than hydride, the masked nucleophile, allyltrimethylsilane, was used in place of triethylsilane (Scheme III). Excellent yields of the appropriate allyl *C*-glycoside(s) were obtained in all reactions attempted (Table V).

The stereochemistry of allyl addition in these *C*-glycosides was determined as follows. Compound **27**, 1-(α-D-glucopyranosyl)-2-propene, was converted to 1-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)propane by sequential hydrogenation and acetylation. The latter product was found to be identical (by 300-MHz ^{1}H NMR) to the compound produced by sequential debenzylation (H_2/Pd-C/MeOH–AcOH) and acetylation (Ac_2O/DMAP–Pyr) of 1-(tetra-*O*-benzyl-α-D-glucopyranosyl)-2-propene.[14] The coupling constants observed for acetylated (Ac_2O/Pyr) compound **27** [$J_{H\text{-}1',2'}$ = 5.7 Hz, $J_{H\text{-}2',3'}$ = 9.5 Hz, $J_{H\text{-}4',5'}$ = 9.4 Hz] also support the assigned stereochemistry.

The assignment of stereochemistry for the three furan compounds (**28**, **29**, **30**) was not as straightforward. In the 300-MHz ^{1}H NMR spectrum of acetylated compound **28**, the H-1′ and H-4′ signals appeared as an unresolved dectet centered at δ 4.22. Decoupling experiments, however, revealed H-1′ to be a doublet of triplets with coupling constants of 3.3 Hz ($J_{H\text{-}1',2'}$) and 7.0 Hz ($J_{H\text{-}1',\text{methylene protons}}$) and H-4′ to be a doublet doublet of doublets with coupling constants of 2.9 Hz ($J_{H\text{-}4',5'}$), 4.8 Hz ($J_{H\text{-}4',5'}$), and 7.7 Hz ($J_{H\text{-}4',3'}$). The stereochemistry of allyl incorporation in acetylated compound **28** was determined by carring out nuclear Overhauser enhancement (NOE) experiments on the allyl methylene hydrogens and H-2′. Decoupling of the allyl methylene hydrogens (H-1) gave rise to an NOE at H-4′ while decoupling at H-2′ clearly gave rise to an NOE at H-1′. These results indicate that allyl attachment is α to the ribofuranosyl ring as shown (see Discussion).



28 29 30

Compounds **29** and **30**, arising as a result of C-glycosylation of methyl β-D-fructofuranoside (which were easily separated by hydroxide exchange resin column chromatography; see Experimental Section) were assigned their respective stereochemistry as their acetylated derivatives on the basis of similar NOE experiments. Decoupling of the allyl methylene (H-1) in acetylated compound **29** gave rise to a pronounced NOE at H-3′ while decoupling of the allyl methylene in acetylated compound **30** showed no such effect. Thus, compound **29** was assigned the C-allylated 2,5-anhydro-D-glucitol structure and compound **30**, the C-allylated 2,5-anhydro-D-mannitol structure.

(14) Lewis, M. D.; Cha, J. K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976–4978.

Table IV. Silylation/Reductive Cleavage of Selected Aldoses and Disaccharides[a]

starting material	products[b] compound	yield, %
D-glucose[c]	1,5-anhydro-D-glucitol (**5**)	66
	1,4-anhydro-D-glucitol (**6**)	34
L-arabinose[c]	1,4-anhydro-L-arabinitol (**14**)	82
	1,5-anhydro-L-arabinitol (**26**)	18
sucrose	2,5-anhydro-D-mannitol (**16**)	45
	2,5-anhydro-D-glucitol (**17**)	5
	1,5-anhydro-D-glucitol (**5**)	3
	D-glucose	47
α,α-trehalose[c]	no reaction	

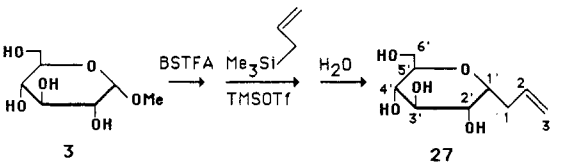
[a] See Experimental Section. [b] Analysis performed on the peracetylated derivatives by GLC, except for sucrose products, which were analyzed by ^{13}C NMR. [c] Reductive cleavage carried out at 80 °C.

Table V. Synthesis of Allyl *C*-Glycosides from Alkyl Glycosides

starting material	product	yield,[a] %
methyl α-D-glucopyranoside (**3**)	1-(α-D-glucopyranosyl)-2-propene (**27**)	88
methyl α,β-D-ribofuranoside (**11a,b**)	1-(α-D-ribofuranosyl)-2-propene (**28**)	96
methyl β-D-fructofuranoside (**15b**)	1-(α-D-fructofuranosyl)-2-propene (**29**)	60
	1-(β-D-fructofuranosyl)-2-propene (**30**)	40

[a] Analysis performed on the peracetylated derivatives by GLC.

Scheme III



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Discussion

Silylation offers a number of advantages as a protection method for the synthesis of anhydroalditols by reductive cleavage: (1) silyl derivatives are easy to prepare; (2) deprotection can often be accomplished simply by aqueous workup, and (3) silyl ethers are only weakly electronegative and thus less likely to destabilize the intermediate cyclic oxonium ion. Indeed, reductive cleavage of independently silylated methyl glycosides (**1** and **2**) gave the appropriate anhydroalditol in excellent yield after aqueous workup.

While silylation proved to be adequate protection during reductive cleavage, the need to carry out separate protection and isolation of the silyl-protected glycoside was still undesirable. A new method was therefore developed in which the reductive cleavage reagents were added directly to the silylation reaction. Both bis(trimethylsilyl)acetamide (BSA) and bis(trimethylsilyl)trifluoroacetamide (BSTFA) readily accomplished silylation, but better yields of anhydroalditols were obtained upon sub-

sequent reductive cleavage when silylation was performed with BSTFA. In general, hexopyranosides and pentofuranosides gave excellent yields of the appropriate anhydroalditol, i.e., pyranosides produced 1,5-anhydroalditols and furanosides produced 1,4-anhydroalditols (Table I). Rearrangement was clearly apparent, however, for methyl β-D-arabinopyranoside (18) and methyl β-D-fructopyranoside (22), which both lack the exocyclic siloxymethyl substituent at the δ-position of the pyran ring, and for methyl α-D-glucoseptanoside (23), which also lacks the exocyclic siloxymethyl substituent. It is possible that the absence of the bulky siloxymethyl substituent allows equilibration among conformers of the intermediate cyclic oxonium ion and collapse, via the appropriate conformer, to a bicyclic anhydroaldose derivative. The latter could subsequently undergo ring opening to produce the more stable five-membered ring oxonium ion, which upon reduction, would yield a 1,4-anhydroalditol. To cite a precedent for this proposal, the 1,4-anhydro-α-arabinopyranose ring system has been shown to undergo acid-catalyzed ring opening in a direction dependent upon reaction conditions.[15] The use of bulkier or more electronegative protecting groups (Table III) helped prevent ring contraction, probably as a result of reduced steric accessibility of the oxygen atom of the siloxy group at the γ-position of the pyran or septan ring and/or higher energy differences between conformers of the cyclic oxonium ion.

The free sugars (D-glucose and L-arabinose) that were subjected to sequential silylation and reductive cleavage also gave anhydroalditols in high yields, but in these cases, mixtures of 1,4- and 1,5-anhydroalditols were formed. In cases where the isomeric anhydroalditols are easily separated, this is a convenient means to prepare 1,4-anhydroalditols, rather than beginning with furanosides which are usually more difficult to access.

The ease with which sequential silylation and reductive cleavage was accomplished led to attempts to add the allyl carbon functionality to the anomeric position by replacing triethylsilane with allyltrimethylsilane. Excellent yields of the appropriate allyl C-glycosides were obtained in all three reactions attempted (Table V). Deprotection was accomplished on workup (as usual) and the olefin functionality was completely retained. In contrast, other protection/deprotection schemes have led to the loss of the olefin functionality.[14] Besides the ease with which these reactions were carried out, they are also highly stereoselective. The same stereoselectivity has been seen in similar reactions involving benzylated derivatives,[14,16,17] but the silyl ether protecting group is clearly superior to the benzyl ether protecting group when the free allyl C-glycoside is desired. Sequential silylation and C-allylation should make numerous allyl C-furanosides and -pyranosides readily available.

Experimental Section

General. Melting points were obtained on a Fisher-Johns platform melting point apparatus and are uncorrected. Optical rotations were measured at the sodium D line on a Perkin-Elmer Model 241 polarimeter.

NMR spectra were obtained on a Nicolet NT-300 spectrometer. ^1H and ^{13}C spectra were recorded at 300 MHz and 75.46 MHz, respectively. Spectra, obtained with either C^2HCl_3 or $C_6{}^2H_6$ as solvent, were referenced to internal tetramethylsilane, and spectra obtained with ^2H_2O as solvent were referenced to internal sodium 3-(trimethylsilyl)-2,2′,3,3′-tetradeuteriopropionate (TSP). ^{13}C spectra were obtained with broad-band proton decoupling. The ^{13}C NMR chemical shift of 1,4-dioxane in ^2H_2O was found to be 69.36 ppm downfield from TSP, and this value was used to correct those cited ^{13}C spectra which were obtained in ^2H_2O with 1,4-dioxane as an internal standard but referenced to external CS_2.

Analytical GLC was performed (a) on a Hewlett-Packard F and M Model 810 chromatograph equipped with a flame ionization detector (FID) and a stainless steel column (3.18 mm × 2.44 m) of 10% of SP2401 on 100-120 Supelcoport. The temperature was held constant at 220 °C; (b) on a Perkin-Elmer Model Sigma 3B capillary chromatograph equipped with a flame-ionization detector, a Hewlett-Packard Model 3390A integrator, and a glass capillary column (0.2 mm × 30 m) of OV101. The temperature was held at 50 °C for 4 min and then was programmed to 180 °C at 10°/min and was then held at 180 °C; (c) on a Hewlett-Packard Model 5890 gas chromatograph equipped with a Hewlett-Packard Model 3892A integrator, a flame ionization detector, and a glass capillary column (0.2 mm × 25 m) of cross-linked methyl silicone (SE-30 equivalent). The temperature was held at 140 °C for 5 min, programmed to 180 °C at 5°/min, and then held at 180 °C; (d) as in method c, except that the temperature was held at 150 °C for 5 min, programmed to 240 °C at 10°/min, and then held at 240 °C.

GLC-MS analyses were performed with a Finnigan 4000 mass spectrometer equipped with a VG Multispec data system. Column effluents were analyzed by chemical ionization (CI) mass spectrometry (MS) (GLC-CIMS) with ammonia as the reagent gas, wherein characteristic (M + 1) and (M + 18) ions were detected, and by electron-impact (EI) MS (GLC-EIMS), in order to aid in structural identification. Elemental analyses were performed by M-H-W Laboratories, Inc., Phoenix, AZ.

Triethylsilane (Et_3SiH), trimethylsilyl trifluoromethanesulfonate (TMSOTf), triethylsilyl trifluoromethanesulfonate (Et_3SiOTf), allyltrimethylsilane, trifluoromethanesulfonic acid (triflic acid), bis(trimethylsilyl)acetamide (BSA), bis(trimethylsilyl)trifluoroacetamide (BSTFA), *tert*-butyldimethylsilyl chloride, chloro(chloromethyl)dimethylsilane, chlorotriethylsilane, and chlorotrimethylsilane were obtained from Aldrich Chemical Co. TMSOTf and Et_3SiOTf were stored in sealed ampules under argon or dry nitrogen. Dowex AG 501 X-8(D) and AG 1-X8 resins were obtained from Bio-Rad Laboratories.

Sequential Silylation/Reductive Cleavage. The glycoside (0.04–2.0 g) was weighed into a dry flask and reagent grade acetonitrile (1 mL/g of glycoside) and a stir bar were added. Bis(trimethylsilyl)trifluoroacetamide (BSTFA), (0.75 equiv/equiv of hydroxyl) was added and the reaction vessel was sealed and stirred at 78–80 °C until the mixture was clear and uniform. Silylation times varied with the carbohydrate used, with free sugars and disaccharides requiring much more time than the alkyl glycosides. On the average, silylation mixtures were completely clear within 3 h (sucrose was thoroughly ground prior to silylation). The mixture was cooled to room temperature and 5 equiv (per equiv of glycoside) of triethylsilane (or allyltrimethylsilane, for C-glycoside synthesis) were added directly to the silylation mixture, followed by 5 equiv of trimethylsilyl trifluoromethanesulfonate (TMSOTf). The reaction vessel was sealed and stirred at room temperature overnight.

Reactions were worked up by pouring into 5–100 mL of H_2O with stirring (quenchings were performed in a well ventilated hood). Dowex AG 501-X8(D) mixed bed exchange resin was added slowly with stirring until its blue color was retained, and the resin was filtered and washed with water to give a clear aqueous filtrate. Evaporation of the filtrate to dryness under vacuum provided a clear, colorless syrup which would often crystallize spontaneously.

Acetylation. Acetylation was accomplished by stirring in a mixture of 2:1 (v/v) pyridine/acetic anhydride (5-fold excess) overnight at room temperature. The reaction was quenched with water (one equivalent volume) at 0–5 °C, and after 10 min of stirring was diluted with CH_2Cl_2 and washed successively with 2 N sulfuric acid, saturated aqueous sodium hydrogen carbonate, and water. After drying over anhydrous sodium sulfate, the CH_2Cl_2 solution was carefully evaporated under vacuum at 25 °C.

Silylations. Silylations (other than with BSTFA or BSA) were carried out according to Oglivie et al.[18] by using silyl chloride and

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imidazole in dimethylformamide. The reactions were monitored by removal of aliquots and analysis by GLC (method a) to ensure complete silylation. Products were isolated by using aqueous quenching and extraction with diethyl ether. Complete silylation of the isolated products was confirmed by integrated ^1H NMR analysis. The trimethylsilylated glucopyranosides (**1** and **2**) were synthesized and distilled according to Hedgley and Overend.[19]

Preparations. Methyl α-D-glucopyranoside (**3**) was obtained from Eastman Organic Chemical Co. Methyl β-D-glucopyranoside (**4**), D-ribrose, and α,α-trehalose were obtained from Pfanstiehl Laboratories, Inc. Methyl α-D-mannopyranoside (**7**), methyl α-D-galactopyranoside (**9a**), methyl β-D-arabinopyranoside (**18**), and L-arabinose were obtained from Sigma Chemical Co. D-Fructose was obtained from Spectrum Chemical Mfg. Corp. Methyl α,β-D-ribofuranoside (**11a,b**) was prepared from D-ribose according to the procedure of Barker and Fletcher.[20] Methyl α-L-arabinofuranoside (**13a**) and methyl β-L-arabinofuranoside (**13b**) were isolated from a mixture of methyl L-arabinoglycosides (prepared from L-arabinose according to Fletcher[21]) by using a column of AG 1-X8 (OH^- form, 200–400 mesh).[22] Methyl α-D-fructofuranoside (**15a**), methyl β-D-fructofuranoside (**15b**), and methyl β-D-fructopyranoside (**22**) were prepared from D-fructose and isolated according to Angyal et al.[22] Benzyl β-D-arabinopyranoside (**21**) was prepared according to the procedure of McCormick.[23] Methyl α-D-glucoseptanoside (**23**) was prepared from 6-*O*-benzoyl-2,3:4,5-di-*O*-isopropylidine-D-glucose diethyl dithioacetal (courtesy of M. Y. H. Wong[24]) according to the method of Ng and Stevens.[25] Glycosides were checked for purity by peracetylation followed by GLC (method a) and NMR (^1H and/or ^{13}C) analysis. Methyl 2,3,4-tri-*O*-methyl-β-D-arabinopyranoside (**24**) was prepared by Hakomori[26,27] methylation of methyl β-D-arabinopyranoside and the structure was confirmed by ^1H NMR.[28]

1,5-Anhydro-D-glucitol (5). Sequential silylation/reductive cleavage of 0.1–1.0 g of either methyl α- or β-D-glucopyranoside (**3** or **4**) produced compound **5** as a crystalline material. Recrystallization from MeOH[8] gave pure 1,5-anhydro-D-glucitol in 75–90% overall yield: mp 142–143 °C (lit.[8] mp 140–141 °C); $[\alpha]^{22}_D$ +41.1° (lit.[8] $[\alpha]^{20}_D$ +42.4°); ^{13}C NMR (Me_2SO-d_6) δ 61.5, 69.6, 69.9, 70.4, 78.5, 81.6 [lit.[29] (^2H_2O): δ 60.2, 68.5, 69.1, 69.4, 77.1, 80.0].

[2,3,4,6-Tetra-*O*-acetyl-1,5-anhydro-D-glucitol. ^1H NMR (C^2HCl_3): δ 2.03, 2.09 (2 s, 6 H, OAc), 2.04 (s, 6 H, OAc), 3.31 (dd, *J* = 10.6, 11.1 Hz, 1 H, H-1a), 3.60 (ddd, *J* = 2.4, 4.8, 10.0 Hz, 1 H, H-5), 4.13 (dd, *J* = 2.4, 12.4 Hz, 1 H, H-6), 4.15 (dd, *J* = 5.6, 11.1 Hz, 1 H, H-1e), 4.21 (dd, *J* = 4.8, 12.4 Hz, 1 H, H-6′), 5.01 (ddd, *J* = 5.6, 9.5, 10.6 Hz, 1 H, H-2), 5.03 (dd, *J* = 9.4, 10.0 Hz, 1 H, H-4), 5.20 (t, *J* = 9.5 Hz, 1 H, H-3).]

1,4-Anhydro-D-glucitol (6). The mixture of **5** and **6** (2.1 g) produced by sequential silylation/reductive cleavage of D-glucose (2.5 g, see Table IV) was separated by sequential acetonide formation (acetone, H^+), gel-permeation chromatography on Bio-Gel P-2, and hydrolysis. Compound **6** was recrystallized from 2-propanol:[30] mp 116–117 °C (lit.[31] mp 115–116 °C); $[\alpha]^{24}_D$ −23.1° (lit.[31] $[\alpha]^{27}_D$ −21.9°); ^{13}C NMR (^2H_2O) δ 66.4, 71.7, 76.1, 78.5, 79.0, 82.5 [lit.[29] (^2H_2O): δ 65.2, 70.6, 75.0, 77.5, 78.0, 81.5].

[2,3,5,6-Tetra-*O*-acetyl-1,4-anhydro-D-glucitol. ^1H NMR (C^2HCl_3) δ 2.01, 2.07, 2.08, 2.11 (four s, 12 H, OAc), 3.82 (dd, *J* = 1.7, 10.7 Hz, 1 H, H-1), 4.13 (dd, *J* = 5.2, 12.2 Hz, 1 H, H-6), 4.22 (dd, *J* = 3.5, 9.4 Hz, 1 H, H-4), 4.27 (dd, *J* = 4.8, 10.7 Hz, 1 H, H-1′), 4.59 (dd, *J* = 2.4, 12.2 Hz, 1 H, H-6′), 5.09 (complex, 1 H, H-2), 5.19 (ddd, *J* = 2.4, 5.2, 9.4 Hz, 1 H, H-5), 5.43 (d, *J* = 3.5 Hz, 1 H, H-3).]

1,5-Anhydro-D-mannitol (8). Sequential silylation/reductive cleavage of 1.0 g of methyl α-D-mannopyranoside (**7**) produced **8** as a crude crystalline material. Recrystallization from methanol[32] gave 0.78 g of pure **8** (93% overall yield): mp 154–155 °C (lit.[32] mp 155 °C); $[\alpha]^{23}_D$ −50.2° (lit.[32] $[\alpha]^{23}_D$ −50.5°); ^{13}C NMR (^2H_2O) δ 64.0, 70.1, 71.8, 72.6, 76.3, 83.3 [lit.[29] (^2H_2O): δ 62.8, 68.9, 70.7, 71.5, 75.2, 82.2].

[2,3,4,6-Tetra-*O*-acetyl-1,5-anhydro-D-mannitol. ^1H NMR (C^2HCl_3); δ 2.01, 2.05, 2.11, 2.17 (four s, 12 H, OAc), 3.59 (ddd, *J* = 2.4, 5.4, 9.9 Hz, 1 H, H-5), 3.67 (dd, *J* = 1.3, 13.2 Hz, 1 H, H-1a), 4.07 (dd, *J* = 2.1, 13.2 Hz, 1 H, H-1e), 4.14 (dd, *J* = 2.4, 12.3 Hz, 1 H, H-6), 4.24 (dd, *J* = 5.4, 12.3 Hz, 1 H, H-6′), 5.06 (dd, *J* = 3.5, 10.0 Hz, 1 H, H-3), 5.28 (t, *J* = 10.0 Hz, 1 H, H-4), 5.32 (complex, 1 H, H-2).]

1,5-Anhydro-D-galactitol (10). Silylation/reductive cleavage of methyl α- or β-D-galactopyranoside (**9a** or **9b**) produced **10** as a crude crystalline material. Recrystallization from ethanol[33] gave pure **10**: mp 115–117 °C (lit.[33] mp 114–115 °C); $[\alpha]^{21}_D$ +76.2° (lit.[33] $[\alpha]_D$ +76.6°); ^{13}C NMR (^2H_2O) δ 61.9, 67.2, 69.6, 69.7, 74.6, 79.9 [lit.[29] (^2H_2O): δ 61.0, 66.1, 68.8, 68.8, 73.8, 79.1].

[2,3,4,6-Tetra-*O*-acetyl-1,5-anhydro-D-galactitol. ^1H NMR (C^2HCl_3): δ 2.01, 2.05, 2.06, 2.15 (four s, 12 H, OAc), 3.29 (dd, *J* = 10.3, 11.1 Hz, 1 H, H-1a), 3.82 (dt, *J* = 1.2, 6.5 Hz, 1 H, H-5), 4.09 (d, *J* = 6.5 Hz, 2 H, H-6,6′), 4.19 (dd, *J* = 5.5, 11.1 Hz, 1 H, H-1e), 5.04 (dd, *J* = 3.4, 10.2 Hz, 1 H, H-3), 5.22 (dt, *J* = 5.5, 10.3 Hz, 1 H, H-2), 5.44 (dd, *J* = 1.2, 3.4 Hz, 1 H, H-4).]

1,4-Anhydro-D-ribitol (12). Sequential silylation/reductive cleavage of 0.5 g of methyl α,β-D-ribofuranoside (**11a,b**) produced **12** as a crystalline compound upon drying. Recrystallization from 2-propanol[20] produced 0.285 g (70% overall) of 1,4-anhydro-D-ribitol: mp 101–102 °C (lit.[20] 100–101 °C); $[\alpha]^{20}_D$ +61.9° (lit.[20] $[\alpha]^{20}_D$ +67°); ^{13}C NMR (^2H_2O) δ 61.8, 71.5, 72.1, 72.7, 82.0 [lit.[29] (^2H_2O) δ 61.0, 70.6, 71.2, 71.8, 81.4].

[2,3,5-Tri-*O*-acetyl-1,4-anhydro-D-ribitol. ^1H NMR (C^2HCl_3): δ 2.08, 2.09, 2.10((three s, 9 H, OAc), 3.87 (dd, *J* = 3.9, 10.3 Hz, 1 H, H-1a), 4.12 (dd, *J* = 5.0, 11.3 Hz, 1 H, H-5), 4.16 (complex, 1 H, H-4), 4.23 (dd, *J* = 5.2, 10.3 Hz, 1 H, H-1b), 4.33 (complex, 1 H, H-5′), 5.13 (complex, 1 H, H-3), 5.37 (dt, *J* = 3.9, 5.3 Hz, 1 H, H-2).]

2,5-Anhydro-D-mannitol (16). Sequential silylation/reductive cleavage of methyl α- or β-D-fructofuranoside (**15a** or **15b**, Table I) as well as sucrose (Table IV) gave 2,5-anhydro-D-mannitol (**16**) as the major product. The sequential silylation/reductive cleavage of 420 mg of methyl β-D-fructofuranoside (**15b**) produced 350 mg of a mixture of compounds **16** and **17**. A portion (100 mg) of this mixture was partially separated by using a 5 × 1.3 cm boronic acid gel affinity column[35] (Affi-gel 601, Bio-Rad Laboratories) to give 75 mg of **16** and 6 mg of **17** (below). Compound **16** was found to contain 5% of **17** by GLC (method a): $[\alpha]^{25}_D$ +47.2° (lit.[36] $[\alpha]^{25}_D$ +58.2°); ^{13}C NMR (^2H_2O) δ 61.1, 76.3, 82.2 [lit.[29] (^2H_2O): δ 60.6, 76.0, 81.9].

[1,3,4,6-Tetra-*O*-acetyl-2,5-anhydro-D-mannitol. ^1H NMR (C^2HCl_3): δ 2.11 (s, 12 H, OAc), 4.25 (s, 6 H, H-1,1′,2,5,6,6′), 5.16 (s, 2 H, H-3,4).]

2,5-Anhydro-D-glucitol (17). Separation of the mixture of **16** and **17** (above) gave 6 mg of 2,5-anhydro-D-glucitol (**17**) as a clear syrup [GLC (method a) shows 15% of syrup is **16**]. ^{13}C NMR (^2H_2O): δ 60.0, 61.6, 76.8, 77.9, 80.8, 84.5 [lit.[29] (^2H_2O): δ 59.8, 61.3, 76.6, 77.7, 80.6, 84.5].

[1,3,4,6-Tetra-*O*-acetyl-2,5-anhydro-D-glucitol. ^1H NMR (C^2HCl_3): δ 2.08, 2.10, 2.11, 2.12 (four s, 12 H, OAc), 4.06 (ddd, *J* = 3.5, 4.8, 6.3 Hz, 1 H, H-5), 4.16 (ddd, *J* = 3.7, 6.4, 11.3 Hz, 1 H, H-2), 4.22–4.40 (complex, 4 H, H-1,1′,6,6′), 5.00 (dd, *J* = 1.5, 3.5 Hz, 1 H, H-4), 5.32 (dd, *J* = 1.5, 3.7 Hz, 1 H, H-3).]

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1,4-Anhydro-D-arabinitol (19). Sequential silylation/reductive cleavage of 0.15 g of methyl β-D-arabinopyranoside (**18**) produced 0.11 g of a mixture of **19** and **20** (see Table III). Separation on a column (1.5 × 35 cm) of AG-1X8 (200–400 mesh, OH^- form, with H_2O as eluent) gave 5.5 mg of **20** (see below) and 83 mg of **19** as a clear, colorless oil: $[\alpha]_D$ +24.6 (lit.[34] $[\alpha]_D$ +25.3) (both in absolute MeOH); ^{13}C NMR (^2H_2O) δ 64.4, 75.5, 79.6, 80.6, 88.2 [lit.[29] (^2H_2O): δ 63.2, 74.8, 78.6, 79.7, 87.2].

[2,3,5-Tri-*O*-acetyl-1,4-anhydro-D-arabinitol. ^1H NMR (C^2HCl_3): δ 2.10 (s, 3 H, OAc), 2.11 (s, 6 H, OAc), 4.01 (complex, 2 H, H-1, H-4), 4.07 (dd, *J* = 4.1, 10.9 Hz, 1 H, H-1′), 4.21 (dd, *J* = 6.8, 11.6 Hz, 1 H, H-5), 4.36 (dd, *J* = 4.5, 11.6 Hz, 1 H, H-5′), 5.04 (br d, *J* = 3.4 Hz, 1 H, H-3), 5.18 (complex, 1 H, H-2).]

1,5-Anhydro-D-arabinitol (20). Separation of the mixture of 1,4- and 1,5-anhydro-D-arabinitol (**19** and **20**, see **19** above) gave 5.5 mg of **20** as a syrup. ^{13}C NMR (^2H_2O): δ 69.8, 70.9, 71.8, 72.5, 75.5.

[2,3,4-Tri-*O*-acetyl-1,5-anhydro-D-arabinitol. ^1H NMR (C^2HCl_3): δ 2.06, 2.08, 2.12 (3 s, 9 H, OAc), 3.39 (dd, *J* = 7.6, 11.6 Hz, 1 H, H-1), 3.64 (dd, *J* = 2.3, 12.5 Hz, 1 H, H-5), 3.87 (dd, *J* = 4.5, 12.5 Hz, 1 H, H-5′), 4.03 (dd, *J* = 3.8, 11.6 Hz, 1 H, H-1′), 5.14 (complex, 2 H, H-2,4), 5.30 (complex, 1 H, H-3), ($J_{H\text{-}1,1'}$ = 11.6, $J_{H\text{-}1,2}$ = 7.6 $J_{H\text{-}1',2}$ = 3.8, $J_{H\text{-}4,5}$ = 2.3, $J_{H\text{-}4,5'}$ = 4.5, $J_{H\text{-}5,5'}$ = 12.5 Hz) (lit.[37] ($C_6{}^2H_6$): $J_{H\text{-}1,1'}$ = 11.6, $J_{H\text{-}1,2}$ = 8.2, $J_{H\text{-}1',2}$ = 4.6, $J_{H\text{-}4,5}$ = 2.2, $J_{H\text{-}4,5'}$ = 4.3, $J_{H\text{-}5,5'}$ = 12.2 Hz).]

1,5-Anhydro-2,3,4-tri-*O*-methyl-D-arabinitol (25). Compound **24** (16 mg) was treated overnight with 5 equiv of Et_3SiH and 5 equiv of TMSOTf in 0.25 mL of CH_2Cl_2 and then quenched by the addition of aqueous sodium hydrogen carbonate. Analysis of the organic layer by capillary GLC (method c) revealed a single product: GLC-CIMS (NH_3), *m/e* 177 (M + 1), 194 (M + 18); GLC-EIMS, *m/e* 176 (9.9), 117 (7.5), 114 (6.2), 101 (9.2), 88 (30.4), 85 (15.3), 75 (50.6), 58 (100), 45 (38.2), 29 (17.7).

1-(α-D-Glucopyranosyl)-2-propene (27). Sequential silylation/allyl addition [see Sequential Silylation/Reductive Cleavage (above)] of 200 mg of methyl α-D-glucopyranoside (**3**) gave 184 mg (87% yield) of white, crystalline **27**. Recrystallization from EtOH gave white crystals: mp 153–156 °C; ^{13}C NMR (^2H_2O) δ 31.4, 63.4, 72.7, 73.6, 74.9, 75.7, 77.8, 120.0, 137.1. Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 52.96; H, 7.95.

[1-(2′,3′,4′,6′-Tetra-*O*-acetyl-α-D-glucopyranosyl)-2-propene. ^1H NMR (C^2HCl_3): δ 2.03, 2.04, 2.05, 2.08 (four s, 12 H, OAc), 2.29–2.62 (complex, 2 H, H-1), 3.86 (ddd, *J* = 2.7, 5.4, 9.4 Hz, 1 H, H-5′), 4.08 (dd, *J* = 2.7, 12.1 Hz, 1 H, H-6′), 4.11 (dd, *J* = 5.4, 12.1 Hz, 1 H, H-6′), 4.28 (ddd, *J* = 4.6, 5.7, 10.8 Hz, 1 H, H-1′), 4.98 (dd, *J* = 8.8, 9.4 Hz, 1 H, H-4′), 5.09 (dd, *J* = 5.7, 9.5 Hz, 1 H, H-2′), 5.12 (ddd, *J* = 1.3, 2.7, 10.2 Hz, 1 H, H-3), 5.15 (ddd, *J* = 1.5, 2.7, 17.1 Hz, 1 H, H-3), 5.34 (t, *J* = 9.1 Hz, 1 H, H-3′), 5.75 (dddd, *J* = 6.2, 7.3, 10.2, 17.1 Hz, 1 H, H-2).]

1-(α-D-Ribofuranosyl)-2-propene (28). Sequential silylation/allyl addition of 65.3 mg of methyl α,β-ribofuranoside (**11a,b**) gave 55.0 mg (84.2% yield) of a clear, colorless oil (**28**): ^{13}C NMR (^2H_2O) δ 35.8, 64.0, 74.6, 74.7, 82.8, 83.3, 119.9, 136.8.

[1-(2′,3′,5′-Tri-*O*-acetyl-α-D-ribofuranosyl)-2-propene. ^1H NMR (C^2HCl_3): δ 2.04, 2.09, 2.13 (3 s, 9 H, OAc), 2.31–2.50 (complex, 2 H, H-1), 4.10 (dd, *J* = 4.7, 11.7 Hz, 1 H, H-5′), 4.22 (dt, *J* = 3.3, 7.0 Hz, 1 H, H-1′), 4.22 (ddd, *J* = 2.9, 4.8, 7.7 Hz, 1 H, H4′), 4.30 (dd, *J* = 3.0, 11.7 Hz, 1 H, H-5′), 5.07 (ddd, *J* = 1.1, 1.9, 10.2 Hz, 1 H, H-3), 5.10 (ddd, *J* = 1.8, 3.3, 17.1 Hz, 1 H, H-3), 5.27 (dd, *J* = 4.6, 7.8 Hz, 1 H, H-3′), 5.44 (dd, *J* = 3.4, 4.6 Hz, 1 H, H-2′), 5.72 (dddd, *J* = 6.9, 7.0, 10.2, 17.1 Hz, 1 H, H-2). Anal. Calcd for $C_{14}H_{20}O_7$: C, 55.99; H, 6.71. Found: C, 55.76; H, 6.55.]

1-(α-D-Fructofuranosyl)-2-propene (29). Sequential silylation/allyl addition of 206 mg of methyl β-D-fructofuranoside (**15b**) gave 151 mg (70% yield) of a mixture of **29** and **30** as a clear syrup. Complete separation of these two compounds was obtained by using a column (1.5 × 35 cm) of AG-1X8 (200–400 mesh, OH^- form) with H_2O as the eluent. Evaporation of H_2O left 75 mg of **29** and 53 mg of **30** (below) as clear syrups. For compound **29**: ^{13}C NMR (^2H_2O) δ 41.5, 63.5, 66.5, 77.6, 82.2, 82.2, 86.1, 122.1, 134.8.

[1-(1′,3′,4′,6′-Tetra-*O*-acetyl-α-D-fructofuranosyl)-2-propene. ^1H NMR (C^2HCl_3): δ 2.06, 2.08, 2.10, 2.11 (4 s, 12 H, OAc), 2.30 (ddt, *J* = 1.1, 7.3, 14.1 Hz, 1 H, H-1), 2.48 (ddt, *J* = 1.1, 7.3, 14.1 Hz, 1 H, H-1), 3.98 (d, *J* = 11.7 Hz, 1 H, H-1′), 4.09–4.16 (complex, 2 H, H-6′), 4.19 (d, *J* = 11.7 Hz, 1 H, H-1′), 4.36 (dt, *J* = 5.9, 9.8 Hz, 1 H, H-5′), 5.17–5.25 (complex, 2 H, H-3), 5.27 (dd, *J* = 5.3, 5.9 Hz, 1 H, H-4′), 5.40 (d, *J* = 5.3 Hz, 1 H, H-3′), 5.81 (dddd, *J* = 7.3, 7.4, 11.6, 16.6 Hz, 1 H, H-2). Anal. Calcd for $C_{17}H_{24}O_9$: C, 54.83; H, 6.49. Found: C, 54.93; H, 6.13.]

1-(β-D-Fructofuranosyl)-2-propene (30). **30** was prepared as above (see compound **29**). ^{13}C NMR (^2H_2O): δ 39.5, 64.4, 66.6, 78.3, 80.5, 83.0, 86.7, 121.4, 136.0.

[1-(1′,3′,4′,6′-Tetra-*O*-acetyl-β-D-fructofuranosyl)-2-propene. ^1H NMR (C^2HCl_3): δ 2.10, 2.11 (two s, 6 H, OAc), 2.12 (s, 6 H, OAc), 2.32 (ddt, *J* = 1.0, 7.9, 14.4 Hz, 1 H, H-1), 2.43 (ddt, *J* = 1.3, 6.4, 14.4 Hz, 1 H, H-1), 4.14 (complex, 4 H, H-1′,6′), 4.33 (complex, 1 H, H-5′), 5.07–5.17 (complex, 2 H, H-3), 5.21 (dd, *J* = 4.2, 5.9 Hz, 1 H, H-4′), 5.38 (d, *J* = 4.3 Hz, 1 H, H-3′), 5.79 (dddd, *J* = 6.4, 7.9, 10.5, 16.8 Hz, 1 H, H-2). ^1H NMR ($C_6{}^2H_6$): δ 1.58, 1.59, 1.65, 1.66 (four s, 12 H, OAc), 2.30–2.53 (complex, 2 H, H-1), 4.13–4.20 (complex, 2 H, H-6′), 4.24 (d, *J* = 11.4 Hz, 1 H, H-1′), 4.29 (d, *J* = 11.4 Hz, 1 H, H-1′), 4.38 (complex, 1 H, H-5′), 5.1–5.5 (complex, 2 H, H-3), 5.38 (dd, *J* = 4.1, 5.1 Hz, 1 H, H-4′), 5.62 (d, *J* = 4.1 Hz, 1 H, H-3′), 5.90 (complex, 1 H, H-2).]

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Preparation and Assignment of Configuration of *cis*- and *trans*-2,3,4,4a,5,6-Hexahydro-2-naphthalenol

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The two diastereomers of 2,3,4,4a,5,6-hexahydro-2-naphthalenol (*cis*-1-OH and *trans*-1-OH) have been prepared and configurations have been established by correlation with the diastereomeric 9-methyldecalins (**8**). The correlations also establish configurations of the diastereomeric 3,4,4a,5,6,8a-hexahydro-8a-methylnaphthalenes (**2**). Configurations have also been established for the isomeric 2,3,4,4a,5,6-hexahydro-2-methylnaphthalenes (**3**) by correlation with the corresponding 2-methyldecalins.

In other projects we have investigated solvolytic and cross-coupling reactions in the 2,3,4,4a,5,6-hexahydro-2-naphthalenyl system (**1**). This paper reports the preparations and assignment of configurations of the two diastereomeric alcohols *cis*-1-OH and *trans*-1-OH.[1] The correlations involved in the structural assignments also establish configurations for the diastereomeric

(1) The cis–trans designation refers to the substituents (or hydrogens) at C-2 and C-4a.

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