till all the diethylammonium trichloromethanesulfonate salt precipitated, while the azaphosphetine cation **3d** remained in solution. Evaporation of the solution afforded **3d** as a brown oil.

**3d**: yield 50%. $^{31}P$ NMR ($CDCl_3$): $\delta$ 132.4 ppm. $^1H$ NMR ($CDCl_3$): $\delta$ 1.00 (t, $^3J_{HH}$ = 7 Hz, 3 H, $CH_3CH_2$), 1.12 (t, $^3J_{HH}$ = 7 Hz, 9 H, $CH_3CH_2$), 1.15 [s, 9 H, $C(CH_3)_3$], 1.33 [s, 9 H, $C(CH_3)_3$], 2.6–2.9 (m, 8 H, $CH_2CH_3$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ 11.34 [s, $CN(CH_2CH_3)_2$], 14.0 [s, $CN(CH_2CH_3)_2$], 14.2 [m, $PN(CH_2CH_3)_2$, 30.2 [d, $^4J_{CP}$ = 4.6 Hz, $NC(CH_3)_2$], 31.3 [d, $^4J_{CP}$ = 6.4 Hz, $=NC(CH_3)_3$], 41.9 [d, $^2J_{CP}$ = 13.1 Hz, $PN(CH_2CH_3)_2$], 43.4 [s, $CN(CH_2CH_3)_2$, 46.9 [s, $CN(CH_2CH_3)_2$], 45.8 [d, $^2J_{CP}$ = 45 Hz, $PN(CH_2CH_3)_2$], 58.65 [d, $^3J_{CP}$ = 6.4 Hz, $>NC(CH_3)_3$], 63.58 [d, $^3J_{CP}$ = 1 Hz, $=NC(CH_3)_3$], 120.83 (q, $^1J_{CF}$ = 319.7 Hz, $CF_3SO_3^-$, 158.59 (d, $^1J_{CP}$ = 14.5 Hz, $PC<$), 160.44 (d, $^1J_{CP}$ = 19.4 Hz, $PC=N$) ppm. $^{19}F$ NMR ($CDCl_3$): $\delta$ −0.25 (s, $CF_3SO_3^-$) ppm. IR ($CDCl_3$): 1670, 1600 ($\nu$ C=N) $cm^{-1}$. Anal. Calcd for $C_{19}H_{38}F_3N_4O_3PS$: C, 46.52; H, 7.81; N, 11.42. Found: C, 46.18; H, 7.71; N, 11.21.

**Addition of *tert*-Butyl Isocyanide to Bis(diisopropylamino)phosphenium Trifluoromethanesulfonate.** A solution of *tert*-butyl isocyanide (0.831 g, 0.01 mol) in dichloromethane (10 mL) was slowly added at −78 °C to a solution of bis(diisopropylamino)phosphenium trifluoromethanesulfonate (1.900 g, 0.005 mol) in dichloromethane (10 mL). At the end of the addition, the resulting mixture was immediately concentrated to dryness. The residue thus obtained was treated with 4 × 15 mL of pentane. The insoluble portion contained the (diisopropylamino)cyanophosphenium trifluoromethanesulfonate as a brown oil while evaporation of the pentane solution afforded bis(diisopropylamino)cyanophosphine (**5**) as a white powder.

**5**: yield 50%. $^{31}P$ NMR ($CDCl_3$): $\delta$ 36 ppm. $^1H$ NMR ($CDCl_3$): $\delta$ 1.2 (d, $^3J_{HH}$ = 6.5 Hz, 24 H, $CH_3$), 3.5 (m, 4 H, C*H*) ppm. IR ($CDCl_3$): 2180 ($\nu$ C≡N) $cm^{-1}$. MS: *m/e* 257 ($M^+$), 231 ($M^+$ − CN), 157 ($M^+$ − $NPr^i_2$). Anal. Calcd for $C_{13}H_{28}N_3P$: C, 60.67; H, 10.97; N, 16.32. Found: C, 60.58; H, 10.88; N, 16.27.

The same reaction performed at room temperature led after similar workup to (diisopropylamino)dicyanophosphine (**4**) obtained as a white powder.

**4**: yield 40%. $^{31}P$ NMR ($CDCl_3$): $\delta$ −21 ppm. $^1H$ NMR ($CDCl_3$): $\delta$ 1.23 (d, $^3J_{HH}$ = 7 Hz, 12 H, $CH_3$), 3.7 (m, 2 H, C*H*) ppm. IR ($CDCl_3$): 2180 ($\nu$ C≡N) $cm^{-1}$. Anal. Calcd for $C_8H_{14}N_3P$: C, 52.45; H, 7.70; N, 22.94. Found: C, 52.41; H, 7.61; N, 22.87.

**Reaction of Bis(diisopropylamino)cyanophosphine (5) with tBuNC in the Presence of Triflic Acid.** To a solution of bis(diisopropylamino)cyanophosphine (**5**, 1.29 g, 0.005 mol) in dichloromethane (10 mL) were added triflic acid (0.750 g, 0.005 mol) and then a solution of *tert*-butyl isocyanide (0.416 g, 0.005 mol) in dichloromethane at room temperature. After stirring for 2 h, the solvent was evaporated. The resulting oil was dissolved in dichloromethane (2 mL) and maintained at −20 °C overnight. The ammonium salt precipitated while (diisopropylamino)dicyanophosphine (**4**, 60%) remained in solution and was treated as above.

**Reaction of (Diisopropylamino)cyanophosphenium Salt 6 with tBuNC.** To a solution of (diisopropylamino)cyanophosphenium salt **6**[12] in dichloromethane (1.531 g, 0.005 mol) was added a solution of *tert*-butyl isocyanide (0.416 g, 0.005 mol) in dichloromethane (10 mL) at room temperature. After stirring for 4 h, the solvent was evaporated and the resulting oil treated as above. (Diisopropylamino)dicyanophosphine (**4**) was obtained in 90% yield.

**Registry No.** **1a**, 122947-19-7; **1b**, 100084-30-8; **1d**, 114706-85-3; **1f**, 114684-87-6; **2a**, 7188-38-7; **2c**, 931-53-3; **3a**, 122947-21-1; **3b**, 123001-74-1; **3c**, 122947-23-3; **3d**, 122947-25-5; **3e**, 122947-27-7; **3f**, 122947-29-9; **4**, 122947-30-2; **5**, 97135-49-4; **6**, 114684-85-4; **7**, 33326-16-8.

# Organoaluminum-Induced Opening of the Pyranosidic Ring of Benzyl 2-Deoxy-2-*C*-methylpentopyranosides[1]

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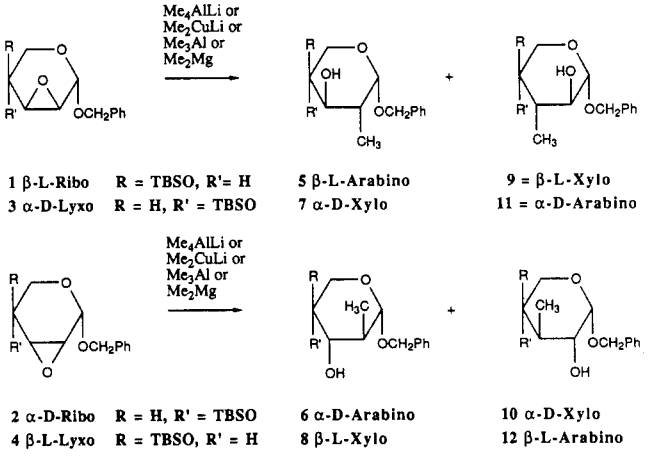
Benzyl 2-deoxy-2-*C*-methylpentopyranosides ring open via attack at the anomeric carbon by the nucleophilic part of organoaluminum reagents ($Me_2AlR$) to give chiral, partially protected, branched 1,2,3,5-tetrol derivatives **13–32**. The reaction represents a direct chain extension of the glycosides at C-1.

We recently reported that the oxirane rings of certain 2,3-anhydropentopyranosides (**1–4**) were regio- and stereoselectively cleaved by organometallic reagents such as $Me_4AlLi$, $Me_2CuLi$, $Me_3Al$, and $Me_2Mg$ to give the branched carbohydrate derivatives **5–8** or **9–12** (Scheme I).[2] The selectivity was controlled by the proper matching of substrate and reagent. We noticed, however, that a side reaction took place when oxirane **1** was treated with $Me_3Al$. This reaction has now been further studied.

When **1** was treated with 1.3 equiv of $Me_3Al$, the deoxymethyl pentosides **5** and **9** were formed in 37% and 11% yield, respectively. Under similar reaction conditions but with 4.0 equiv of $Me_3Al$, neither **5** nor **9** could be detected. Instead, the major product of this reaction turned out to be a 10:1 diastereomeric mixture of the chain-extended tetrol derivatives **13**/**14**[3] (Scheme II). The primary epoxide opening product, i.e. the aluminum alcoholate of **5**, obviously underwent opening of the pyranosidic ring, since pure **5** when treated with 3.0 equiv of $Me_3Al$ gave the same product mixture (**13**/**14**). Similar results were obtained

**Scheme I**



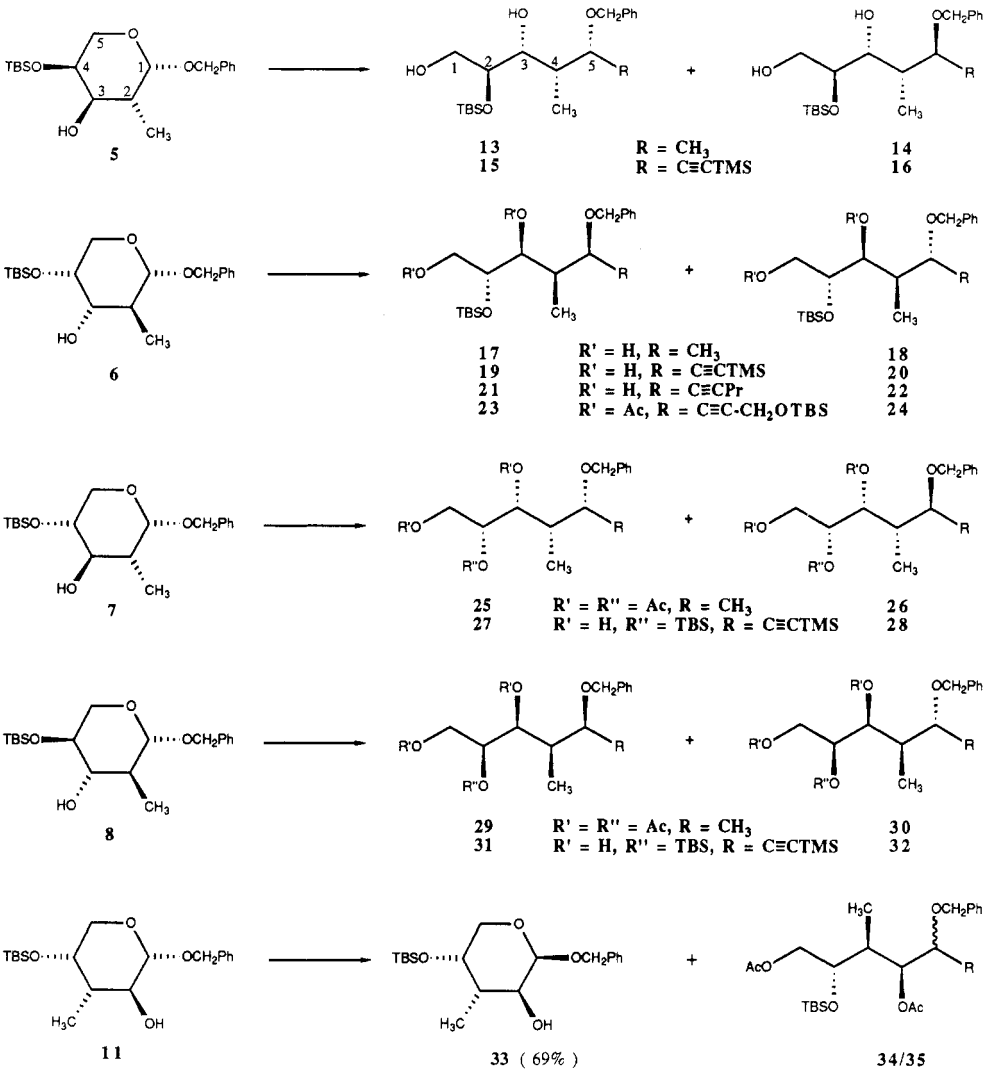

(1) Presented in part at the Seventh IUPAC Conference on Organic Synthesis, July 4–7, 1988, in Nancy, France.

(2) Inghardt, T.; Frejd, T.; Magnusson, G. *J. Org. Chem.* **1988**, *53*, 4542.

(3) There are a few examples in the literature of acetal cleavages by trialkylalanes. See: Takano, S.; Ohkawa, T.; Ogasawara, K. *Tetrahedron Lett.* **1988**, *29*, 1823 and references cited therein.

0022-3263/89/1954-5539$01.50/0 

**Scheme II**




with **6–8**, which all have a "free" 3-OH group.[4] The results are shown in Scheme II and Table I.

The 2-OH compound **10** was essentially unaffected by $Me_3Al$ (3.0 equiv, reflux 18 h) as was the 3-OTBS protected 2-C-$CH_3$ compound **6**. Thus, a free 3-OH group seems necessary for the pyranosidic ring opening to proceed at a convenient rate, but it is not always a requirement since the 2-OH derivative **11** gave **34/35** although in a lower yield. The major process in this case was anomerization to give **33** ($\beta$-D-arabinose configuration).

Under the reaction conditions the hydroxyl group forms an aluminum alcoholate, which is a plausible intermediate in the reaction.[5a] The transfer of methyl groups between dimethylaluminum alcoholates and trialkylalanes is known to be a slow process.[5b] Thus, it is conceivable that the methyl anion equivalent attacking the C-1 position originates from an aluminum species other than that forming the alcoholate. It would then be possible to use first 1 equiv of $Me_3Al$ to form the alcoholate and then a different alane to open up the pyranosidic ring. Indeed, it turned out that acetylenic groups were transferred to C-1 when the preformed dimethylaluminum alcoholate of the 3-OH derivatives **5–8** were added to $Me_2AlC{\equiv}CR$ (R = TMS, $CH_2OTBS$, or $(CH_2)_2CH_3$). In this way we have prepared

**Table I. Result of the Pyranosidic Ring Opening of Deoxy Sugars 5–8 and 11**

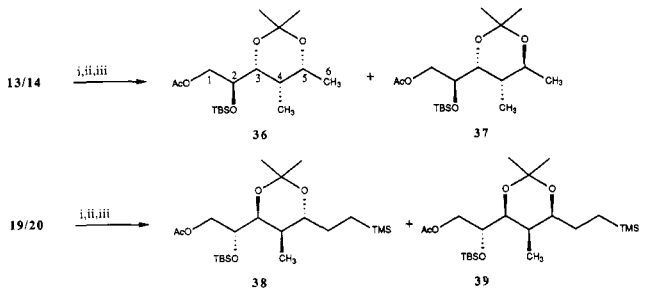
| entry | starting material | conditions[a] | products, ratio[b] | yield,[c] % |
|---|---|---|---|---|
| 1 | **5** | A, refl, 22 h | **13:14**, 10:1 | 46 |
| 2 | | B1, 50 °C, 6 h | **15:16**, <1:20 | 40 |
| 3 | **6** | A, refl, 1 h | **17:18**, 10:1 | 69 |
| 4 | | B1, 50 °C, 1.5 h | **19:20**, <1:20 | 76 |
| 5 | | B2, refl, 2 h | **21:22**, <1:20 | 67 |
| 6 | | B3, 50 °C, 6 h | **23:24**, <1:20 | 38 |
| 7 | **7** | A, refl, 22 h | **25/26**, 1.6:1[d] | 54 |
| 8 | | B1, 50 °C, 6 h | **27/28**, 1:4[d,e] | 28 |
| 9 | **8** | A, refl, 22 h | **29/30**, 1.6:1[d] | 37 |
| 10 | | B1, 50 °C, 1 h | **31/32**, 1:4[d,e] | 67 |
| 11 | **11** | A, refl, 18 h | **34/35**, >25:1[d] | 28[f] |

[a] Condition A: 3 equiv of $Me_3Al$ was added to the starting material. Condition B1-3: 1 equiv of $Me_3Al$ was first added to the starting material followed by 2 equiv of $Me_2AlC{\equiv}CSiMe_3$ (B1), $Me_2AlC{\equiv}C(CH_2)_2CH_3$ (B2), or $Me_2AlC{\equiv}CCH_2OTBS$ (B3). [b] Determined by $^1H$ NMR spectroscopy. [c] Isolated yields. [d] Tentative assignment of diastereomers. [e] Determined by GC of acetylated product. [f] **33** was isolated in 69% yield.

(4) Migration of the TBS group took place to some extent to the primary position of the products in the reaction of **7** and **8** with $Me_3Al$, which made purification difficult. In order to obtain pure compounds the crude product was treated with tetrabutylammonium fluoride followed by acetylation to give the triacetates **25/26** and **29/30**, respectively.

(5) (a) Due to the electron deficiency of aluminum, dialkylaluminum alkoxides form dimers and trimers in noncoordinating solvents, thus reducing the electron density on the oxygen: Mole, T.; Jeffery, E. A. *Aust. J. Chem.* **1968**, *21*, 2683. b) Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 1, p 555. Mole, T.; Jeffery, E. A. *Organoaluminium Compounds*; Elsevier: New York, 1972.

**Scheme III**[a]




[a] (i) $Ac_2O$/pyridine; (ii) $H_2$/Pd–C; (iii) dimethoxypropane, $H^+$.

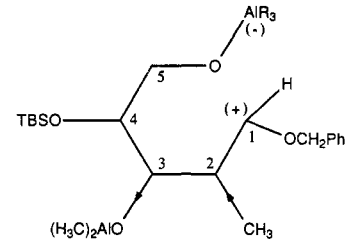
some chiral acetylenic tetrol derivatives (**15/16**, **19/20**, **21/22**, **23/24**, **27/28**, **31/32**), which may lend themselves to further transformations into natural products. Alkenyl groups and alkyl groups other than methyl could not be transferred to C-1 with concomitant opening of the pyranosidic ring.

The stereoselectivities in the formation of the acetylenic tetrols were better than in the corresponding methyl tetrols as seen in Table I. With the exception of **27/28** and **31/32**, the diastereomers were not separable by ordinary silica gel chromatography, whereas analytical separations of the acetylated derivatives were possible using capillary GC.

It was obvious that the products in the reactions of **5** and **6** with $Me_3Al$ were enantiomers based on their identical $^1H$ NMR spectra and their opposite sign of optical rotations. The principal products must then be either **13** and **17** or **14** and **18**. Since they were formed from the diastereomeric starting materials **5** and **6**, which differ diastereotopically at C-1, one of the products must have been formed through a net inversion and the other one through a net retention of the configuration at C-1.

Several approaches may be used in order to settle this matter. We tried first, without success, to obtain crystalline derivatives for X-ray analysis. Nuclear Overhauser enhancement experiments in combination with $^1H$ NMR coupling constants are usually quite informative, but in flexible systems there is considerable ambiguity. Therefore we prepared the acetonides **36/37** and **38/39** (Scheme III), which should be less flexible than the open-chain derivatives, although more than one structure (conformer) may correspond to the same set of coupling constants and NOE data. It is then necessary to estimate which type of ring conformation is dominating in the equilibrium in each case. This estimation was done by using molecular mechanics calculations (MM2(85)).[6] The coupling constants of the favored conformers were then calculated (3JHH)[7] and compared with the experimental values of the acetonides, indicating that **36** and **38** are the major diastereomers. This conclusion was further supported by NOE measurements. Thus the reaction of **5** with $Me_3Al$ proceedes mainly through inversion while the reaction of **6** gives retention of the stereocenter at C-1. When the reagent is changed to $Me_2AlC{\equiv}CR$ the results are the opposite ones, i.e. **5** gives mainly retention and **6** gives inversion for as yet unknown reasons.[8]

Already in 1949 Lindberg suggested that Lewis acid anomerization of $\beta$-glycosides to $\alpha$-glycosides takes place via an open-chain intermediate.[9] It was shown that the aglycons did not cross over in experiments where two glycosides with different aglycons were treated with acid. This indicated that the anomerization proceeded via an opening of the pyranosidic ring followed by a rotation around the C-1–C-2 bond and subsequent ring closure to the thermodynamically most stable glycoside. Since then other authors have interpreted their results in similar ways.[10] Assuming an open-chain intermediate such as **40**, the aluminum–ate complex at the C-5 oxygen may transfer a methyl/alkynyl group intramolecularly to C-1, before or after rotation around the C-1–C-2 bond. At present it is not possible to account for the different stereoselectivities of the two types of reagents, $Me_3Al$ and $Me_2AlC{\equiv}CR$, in the pyranosidic ring-opening reactions.




**40**

Electronic effects may to some extent explain the reluctance of the 2-OH derivatives to undergo ring cleavage. The inductively electron-withdrawing $OAlMe_2$ group would destabilize the intermediate **40** to a larger extent if placed in the 2-position as compared to the 3-position (–I effect).[5] Furthermore, when the methyl group is located at the 2-position its +I effect would help stabilize the positive charge at C-1 in **40** and thus favor the reaction.

We observed that the ring opening of **6** was much faster than that of **5**. NMR data indicate that the preferred conformation of **5** is the $^4C_1$ conformation while for **6** it is the $^1C_4$ conformation.[2] Guindon et al. have pointed out that the complexing ability is greatest for the conformer which does not have an anomeric effect ($^1C_4$ in this case), since here the electron pairs at the ring oxygen do not interact with the orbital system of the glycosidic bond and thus are more available for complex formation.[11] Our results seem to be quite in line with these ideas and are consistent with structure **40** as being a reasonable model of an intermediate.

The reason for the low reactivity of the 3-OTBS derivative of **6** as compared to **6** (3-$OAlMe_2$), is at present unclear. It seems unlikely that the difference is caused by electronic factors, since the developing positive charge at C-1 is located three bonds away from the 3-O substituent.

## Experimental Section

The general procedures were as described in ref 2, with the following additions: A Varian 3700 chromatograph equipped with a RSL 150 (polydimethylsiloxan) capillary column (9 m) was used for GC analyses. Dimethylaluminum chloride (1.0 M in hexanes) was purchased from Aldrich. O-(*tert*-Butyldimethylsilyl)prop-2-ynol was prepared according to ref 12. The deoxymethyl

(6) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society Monograph 177; Washington, DC, 1982. The program is available through QCPE, Department of Chemistry, Indiana University, Bloomington, Indiana 47405, USA.

(7) Osawa, E.; Jaime, C. *QCPE Bull.* **1983**, *3*, 66 (QCPE program no. 461).

(8) In view of their similar values of optical rotation, we conclude that the three alkynyl compounds obtained from **6** have the same C-1 configuration.

(9) Lindberg, B. *Acta Chem. Scand.* **1949**, *3*, 1153.

(10) Morishima, N.; Koto, S.; Zen, S. *Chem. Lett.* **1979**, 749. Köster, R.; Penades-Ullate, S.; Dahlhoff, W. V. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 519. Lichtentaler, F. W.; Breunig, J.; Fischer, W. *Tetrahedron Lett.* **1971**, 2825. Rosenfeld, L.; Ballou, C. E. *Carbohydr. Res.* **1974**, *32*, 287.

(11) Guindon, Y.; Anderson, P. C. *Tetrahedron. Lett.* **1987**, *28*, 2485.

pentopyranosides, **5–8**, **10**, and **11**, were prepared according to ref 2. Column chromatography separations were performed with use of ethyl acetate/heptane (E/H) mixtures as eluents.

**General Methods Used in the Pyranosidic Ring-Opening Reactions.** All reactions involving organometallic reagents were carried out under an argon atmosphere. The dimethylalkynylalanes were prepared by addition of *n*-BuLi (0.98 equiv, 1.51 M in hexane) to the alkyne (0.5 M in hexane) at 0 °C. After 10 min, $Me_2AlCl$ (0.95 equiv, 1.0 M in hexane) was added dropwise, and the mixture was stirred at room temperature for 20 min, prior to the addition of the glycosides. The reaction mixtures were quenched by slow addition with vigorous stirring into cold aqueous ~2 M solutions of $NH_4Cl$ (adjusted to pH ~8 with 2 M $NH_4OH$). The solids were filtered off and thoroughly washed with ethyl acetate. The aqueous phase was extracted with ethyl acetate, and the combined organic phases were washed with water, dried ($Na_2SO_4$), and concentrated in vacuo (12 mmHg, water bath temperature ~35 °C).

Acetylations were carried out by adding the alcohol to a solution of acetic anhydride (2 equiv), pyridine (2 equiv) and 4-pyrrolidinopyridine (0.1 equiv) in dry (4-Å molecular sieves) dichloromethane. After being stirred at room temperature for 24 h, the solution was washed with HCl (0.1 M), saturated aqueous $NaHCO_3$, and water, dried ($Na_2SO_4$), and concentrated in vacuo.

The diastereomeric product ratios were determined from $^1H$ NMR integrals or from GC analysis of the acetylated product mixtures. The NMR data refer to the principal diastereomers unless otherwise indicated.

**Reaction Conditions A.** $Me_3Al$ (3.0 equiv, 2.0 M in hexane) was added to the substrate (0.2 M in hexane) at room temperature. After 10 min, the solution was refluxed for the time indicated in each experiment, cooled (0 °C), and worked up as described above.

**Reaction Conditions B.** The substrate (0.2 M in hexane) was treated with $Me_3Al$ (1.0 equiv, 2.0 M in hexane) at room temperature. After 5 min, this mixture was transferred to a solution of $Me_2AlC{\equiv}CSiMe_3$ (B1), $Me_2AlC{\equiv}C$-Pr (B2), or $Me_2AlC{\equiv}CCH_2OTBS$ (B3) (2.0 equiv, 0.25 M in hexane) at room temperature. After 10 min, the reaction mixture was heated and stirred for the time indicated in each experiment, cooled (0 °C), and worked up as described above.

**(2*S*,3*R*,4*R*,5*R*)- and (2*S*,3*R*,4*R*,5*S*)-5-*O*-Benzyl-4-methyl-2-*O*-(*tert*-butyldimethylsilyl)-1,2,3,5-hexanetetrol (13 and 14).** Benzyl 2-deoxy-2-*C*-methyl-4-*O*-(*tert*-butyldimethylsilyl)-β-L-arabinopyranoside (**5**) (110 mg, 312 μmol) was subjected to reaction conditions A (reflux, 22 h). Column chromatography (E/H, 1:5) of the crude product gave **13/14** (syrup, 53.1 mg, 46%, ratio **13:14** = 10:1): $[\alpha]^{20}_D$ = −32.6° (*c* 0.83, $CHCl_3$); $^1H$ NMR δ 7.32 (m, 5 H, $C_6H_5$), 4.65, 4.39 (AB q, each 1 H, $J_{A,B}$ = 11.4 Hz, $CH_2Ph$), 3.90–3.59 (m, 5 H, H-1, H-1′, H-2, H-3, H-5), 1.88 (m, 1 H, H-2), 1.26 (d, 3 H, $J_{5,6}$ = 6.3 Hz, H-6), 0.97 (d, 3 H, $J_{Me,4}$ = 7.1 Hz, 4-Me), 0.87 (s, 9 H, $Me_3CSi$), 0.10, 0.07 (2 s, each 3 H, $Me_2Si$). Anal. Calcd for $C_{20}H_{36}O_4Si$: C, 65.17; H, 9.84. Found: C, 65.14; H, 9.81.

In order to obtain a well-resolved NMR spectrum, a fraction of the product was acetylated to yield the 1,3-di-*O*-acetates of **13/14**: $^1H$ NMR δ 7.32 (m, 5 H, $C_6H_5$), 5.16 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 4.8 Hz, H-3), 4.57, 4.36 (AB q, each 1 H, $J_{AB}$ = 11.6 Hz, $CH_2Ph$), 4.12, 4.10 (d AB q, each 1 H, $J_{AB}$ = 10.2 Hz, $J_{1,2}$, $J_{1',2}$ = 2.8, 6.2 Hz, H-1, H-1′), 4.08 (m, 1 H, H-2), 3.51 (dq, 1 H, $J_{4,5}$ = 4.7 Hz, H-5), 2.05 (m, 1 H, H-4), 2.02, 1.96 (s, each 3 H, COMe), 1.21 (d, 3 H, $J_{5,6}$ = 6.3 Hz, H-6), 0.98 (d, 3 H, $J_{Me,4}$ = 7.0 Hz, 4-Me), 0.87 (s, 9 H, $Me_3CSi$), 0.06, 0.05 (2 s, each 3 H, $Me_2Si$).

**(2*S*,3*R*,4*R*,5*S*)- and (2*S*,3*R*,4*R*,5*R*)-5-*O*-Benzyl-4-methyl-7-(trimethylsilyl)-2-*O*-(*tert*-butyldimethylsilyl)-hept-6-yne-1,2,3,5-tetrol (15 and 16).** Compound **5** (100 mg, 284 μmol) was subjected to reaction conditions B1 (50 °C, 6 h). Column chromatography (E/H, 1:6) of the crude product gave **15/16** (syrup, 51.7 mg, 40%, ratio **15:16** < 1:20): $[\alpha]^{20}_D$ = +69.4° (*c* 0.72, $CHCl_3$); IR (film) 3540 (OH), 2180 (C≡C) $cm^{-1}$; $^1H$ NMR δ 7.34 (m, 5 H, $C_6H_5$), 4.83, 4.62 (AB q, each 1 H, $J_{A,B}$ = 11.7 Hz, $CH_2Ph$), 4.23 (dd, 1 H, $J_{2,3}$ = 8.3 Hz, H-3), 4.16 (d, 1 H, $J_{4,5}$ = 3.2 Hz, H-5), 3.72 (m, 2 H, H-1, H-1′), 3.61 (m, 1 H, H-2), 2.96, 2.66 (br s, each 1 H, OH), 2.15 (m, 1 H, $J_{3,4}$ = 1.6 Hz, H-4), 1.05 (d, 3 H, $J_{Me,4}$ = 7.2 Hz, 4-Me), 0.88 (s, 9 H, $Me_3CSi$), 0.20 (s, 9 H, $Me_3Si$), 0.10, 0.07 (2 s, each 3 H, $Me_2Si$). Anal. Calcd for $C_{24}H_{42}O_4Si_2$: C, 63.95; H, 9.39. Found: C, 63.78; H, 9.38.

**(2*R*,3*S*,4*S*,5*S*)- and (2*R*,3*S*,4*S*,5*R*)-5-*O*-Benzyl-4-methyl-2-*O*-(*tert*-butyldimethylsilyl)-1,2,3,5-hexanetetrol (17 and 18).** Benzyl 2-deoxy-2-*C*-methyl-4-*O*-(*tert*-butyldimethylsilyl)-α-D-arabinopyranoside (**6**) (100 mg, 284 μmol) was subjected to reaction conditions A (reflux, 1 h). Column chromatography (E/H, 1:3) of the crude product gave **17/18** (syrup, 71.7 mg, 69%, ratio **17:18** = 10:1): $[\alpha]^{20}_D$ = +32.6° (*c* 0.96, $CHCl_3$). The $^1H$ NMR spectra of **17/18** and their 1,3-di-*O*-acetates were identical with the spectra of compounds **13/14** and their 1,3-di-*O*-acetates. Anal. Calcd for $C_{20}H_{36}O_4Si$: C, 65.17; H, 9.84. Found: C, 65.14; H, 10.04.

**(2*R*,3*S*,4*S*,5*R*)- and (2*R*,3*S*,4*S*,5*S*)-5-*O*-Benzyl-4-methyl-7-(trimethylsilyl)-2-*O*-(*tert*-butyldimethylsilyl)-hept-6-yne-1,2,3,5-tetrol (19 and 20).** Compound **6** (500 mg, 1.42 mmol) was subjected to reaction conditions B1 (50 °C, 1.5 h). Column chromatography (E/H, 1:5) of the crude product gave **19/20** (syrup, 484 mg, 76%, ratio **19:20** < 1:20): $[\alpha]^{20}_D$ = −71.6° (*c* 0.76, $CHCl_3$). The IR and $^1H$ NMR spectra of **19/20** were identical with the spectra of compounds **15/16**. Anal. Calcd for $C_{24}H_{42}O_4Si_2$: C, 63.95; H, 9.39. Found: C, 63.73; H, 9.84.

**(2*R*,3*S*,4*S*,5*R*)- and (2*R*,3*S*,4*S*,5*S*)-5-*O*-Benzyl-4-methyl-2-*O*-(*tert*-butyldimethylsilyl)dec-6-yne-1,2,3,5-tetrol (21 and 22).** Compound **6** (50 mg, 142 μmol) was subjected to reaction conditions B2 (reflux, 2 h). Column chromatography (E/H, 1:3) of the crude product gave **21/22** (syrup, 40 mg, 67%, ratio **21:22** < 1:20): $[\alpha]^{20}_D$ = −61.8° (*c* 1.21, $CHCl_3$); IR (film) 3500 (OH), 2240 weak (C≡C) $cm^{-1}$; $^1H$ NMR δ 7.33 (m, 5 H, $C_6H_5$), 4.83, 4.45 (AB q, each 1 H, $J_{A,B}$ = 11.7 Hz, $CH_2Ph$), 4.26 (dd, 1 H, $J_{2,3}$ = 8.4 Hz, $J_{3,4}$ = 1.6 Hz, H-3), 4.18 (dt, 1 H, $J_{4,5}$ = 3.2 Hz, $J_{5,8}$ = 2.0 Hz, H-5), 3.72 (AB q, 2 H, H-1, H-1′), 3.61 (m, 1 H, H-2), 2.24 (dt, 2 H, $J_{8,9}$ = 6.9 Hz, H-8), 2.12 (m, 1 H, $J_{4,Me}$ = 7.1 Hz, H-4), 1.56 (m, 2 H, H-9), 1.05 (d, 3 H, 4-Me), 1.01 (t, 3 H, $J_{9,10}$ = 7.5 Hz, H-10), 0.88 (s, 9 H, $Me_3CSi$), 0.10, 0.07 (2 s, each 3 H, $Me_2Si$). Anal. Calcd for $C_{24}H_{40}O_4Si$: C, 68.53; H, 9.58. Found: C, 68.66; H, 9.73.

**(2*R*,3*S*,4*R*,5*R*)- and (2*R*,3*S*,4*R*,5*S*)-1,3-Di-*O*-acetyl-5-*O*-benzyl-4-methyl-2,8-di-*O*-(*tert*-butyldimethylsilyl)oct-6-yne-1,2,3,5,8-pentol (23 and 24).** Compound **6** (100 mg, 284 μmol) was subjected to reaction conditions B3 (50 °C, 6 h). Due to difficulties in the purification of the diols, the crude products were acetylated. Column chromtography (E/H, 1:6) gave the diacetates **23/24** (syrup, 65.9 mg, 38%, ratio **23:24** < 1:20): $[\alpha]^{20}_D$ = −38.4° (*c* 1.58, $CHCl_3$); IR ($CCl_4$) 2310 very weak (C≡C), 1740 (C=O) $cm^{-1}$; $^1H$ NMR δ 7.34 (m, 5 H, $C_6H_5$), 5.27 (dd, 1 H, $J_{2,3}$, $J_{3,4}$ = 3.5, 5.0 Hz, H-3), 4.77, 4.44 (AB q, each 1 H, $J_{A,B}$ = 11.3 Hz, $CH_2Ph$), 4.39 (d, 2 H, $J_{5,8}$ = 1.6 Hz, H-8), 4.10–3.95 (m, 4 H, H-1, H-1′, H-2, H-5), 2.23 (m, 1 H, H-4), 2.01, 1.98 (2 s, each 3 H, COMe), 1.08 (d, 3 H, $J_{Me,4}$ = 7.0 Hz, 4-Me), 0.92, 0.87 (2 s, each 9 H, $Me_3CSi$), 0.14, 0.06 (s, each 3 H, $Me_2Si$). Correct elemental analysis could not be obtained for **23/24**.

**(2*R*,3*R*,4*S*,5*R*/*S*)-1,2,3-Tri-*O*-acetyl-5-*O*-benzyl-4-methyl-1,2,3,5-hexanetetrol (25/26).** Benzyl 2-deoxy-2-*C*-methyl-4-*O*-(*tert*-butyldimethylsilyl)-α-D-xylopyranoside (**7**) (100 mg, 284 μmol) was subjected to reaction conditions A (reflux, 22 h). Column chromatography (E/H, 1:6) gave a mixture of diols (56.7 mg, 54%) due to partial migration of the TBS group to the primary hydroxyl group. The diol mixture was desilylated (tetrabutylammonium fluoride, 1.1 equiv in tetrahydrofuran, 30 min, 20 °C), and the crude triol was acetylated. Column chromatography (E/H, 1:4) gave **25/26** (syrup, 58.2 mg, 54%, diastereomeric ratio 1.6:1): $[\alpha]^{20}_D$ = +21.0° (*c* 0.70, $CHCl_3$); $^1H$ NMR δ 7.33 (m, 5 H, $C_6H_5$), 5.33 (dd, 1 H, $J_{2,3}$, $J_{3,4}$ = 4.8, 6.8 Hz, H-3), 5.26 (m, 1 H, H-2), 4.59, 4.36 (AB q, each 1 H, $J_{AB}$ = 11.5 Hz, $CH_2Ph$), 4.20, 3.96 (d AB q, each 1 H, $J_{AB}$ = 11.9 Hz, $J_{1,2}$, $J_{1',2}$ = 4.2, 6.3 Hz, H-1, H-1′), 3.51 (dq, 1 H, $J_{4,5}$ = 4.4 Hz, H-5), 2.05, 2.03, 2.02 (3 s, each 3 H, COMe), 1.82 (m, 1 H, H-4), 1.20 (d, 3 H, $J_{5,6}$ = 6.2 Hz, H-6), 0.99 (d, 3 H, $J_{Me,4}$ = 7.0 Hz, 4-Me). Anal. Calcd for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42. Found: C, 63.13; H, 7.48.

**(2*R*,3*R*,4*R*,5*R*/*S*)-5-*O*-Benzyl-4-methyl-7-(trimethylsilyl)-2-*O*-(*tert*-butyldimethylsilyl)hept-6-yne-1,2,3,5-tetrol (27/28).** Compound **7** (100 mg, 284 μmol) was subjected to reaction conditions B1 (50 °C, 6 h). Column chromatography (E/H,

(12) Wender, P.; Sieburth, S.; Petraitis, J.; Singh, S. *Tetrahedron* **1981**, *37*, 3967.

1:7) gave **27/28** (syrup, 35.4 mg, 28%, diastereomeric ratio 4:1 determined by GC after acetylation). The diastereomers were partially separable. The major diastereomer had the following properties: $[\alpha]^{20}_D$ = −81.6° (*c* 0.78, $CHCl_3$); IR ($CCl_4$) 3540 (OH), 2180 (C≡C) $cm^{-1}$; $^1H$ NMR δ 7.34 (m, 5 H, $C_6H_5$), 4.79, 4.77 (AB q, each 1 H, $J_{A,B}$ = 11.7 Hz, $CH_2Ph$), 4.08 (d, 1 H, $J_{4,5}$ = 4.9 Hz, H-5), 3.84 (dd, 1 H, $J_{2,3}$ = 4.5 Hz, H-3), 3.74 (m, 1 H, H-2), 3.64, 3.56 (d AB q, each 1 H, $J_{AB}$ = 11.4, $J_{1,2}$, $J_{1',2}$ = 4.4, 4.8, Hz, H-1, H-1'), 1.93 (m, 1 H, $J_{3,4}$ = 5.0 Hz, H-4), 1.15 (d, 3 H, $J_{Me,4}$ = 7.0 Hz, 4-Me), 0.89 (s, 9 H, $Me_3CSi$), 0.21 (s, 9 H, $Me_3Si$), 0.07, 0.05 (2 s, each 3 H, $Me_2Si$). The minor diastereomer had the following properties: $[\alpha]^{20}_D$ = +62.4° (*c* 0.86, $CHCl_3$); IR ($CCl_4$) 3540 (OH), 2180 (C≡C) $cm^{-1}$; $^1H$ NMR δ 7.34 (m, 5 H, $C_6H_5$), 4.81, 4.50 (AB q, each 1 H, $J_{A,B}$ = 11.7 Hz, $CH_2Ph$), 4.10 (d, 1 H, $J_{4,5}$ = 6.5 Hz, H-5), 3.96 (dd, 1 H, $J_{2,3}$ = 5.6 Hz, H-3), 3.76 (m, 1 H, H-2), 3.66, 3.57 (d AB q, each 1 H, $J_{AB}$ = 11.3, $J_{1,2}$, $J_{1',2}$ = 4.4, 4.8, Hz, H-1, H-1'), 1.96 (m, 1 H, $J_{3,4}$ = 3.8 Hz, H-4), 1.07 (d, 3 H, $J_{Me,4}$ = 7.0 Hz, 4-Me), 0.91 (s, 9 H, $Me_3CSi$), 0.20 (s, 9 H, $Me_3Si$), 0.11, 0.09 (2 s, each 3 H, $Me_2Si$). Anal. Calcd for $C_{24}H_{42}O_4Si_2$: C, 63.95; H, 9.39. Found: C, 63.83; H, 9.39.

**(2*S*,3*S*,4*R*,5*R*/*S*)-1,2,3-Tri-*O*-acetyl-5-*O*-benzyl-4-methyl-1,2,3,5-hexanetetrol (29/30).** Benzyl 2-deoxy-2-*C*-methyl-4-*O*-(*tert*-butyldimethylsilyl)-β-L-xylopyranoside (**8**) (106 mg, 301 μmol) was subjected to reaction conditions A (reflux, 22 h), desilylated, and acetylated as described in the preparation of **25/26**. The triacetate **29/30** (syrup, 41.9 mg, 37%, diastereomeric ratio 1:1.6) had the following: $[\alpha]^{20}_D$ = −22.0° (*c* 1.01, $CHCl_3$). The $^1H$ NMR spectrum of **29/30** was identical with the spectrum of **25/26**. Anal. Calcd for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42. Found: C, 63.02; H, 7.44.

**(2*S*,3*S*,4*S*,5*R*/*S*)-5-*O*-Benzyl-4-methyl-7-(trimethylsilyl)-2-*O*-(*tert*-butyldimethylsilyl)hept-6-yne-1,2,3,5-tetrol (31/32).** Compound **8** (94 mg, 267 μmol) was subjected to reaction conditions B1 (50 °C, 1 h). Column chromatography (E/H, 1:7) gave **31/32** (syrup, 80.3 mg, 67%, diastereomeric ratio 1:4 determined by GC after acetylation). The major diastereomer had the following: $[\alpha]^{20}_D$ = +82.6° (*c* 1.06, $CHCl_3$). The minor diastereomer had the following: $[\alpha]^{20}_D$ = −61.9° (*c* 0.64, $CHCl_3$). The IR and $^1H$ NMR spectra of the two diastereomers **31** and **32** were identical with the spectra of **27** and **28**. Anal. Calcd for $C_{24}H_{42}O_4Si_2$: C, 63.95; H, 9.39. Found: C, 63.79; H, 9.51.

**Benzyl 3-Deoxy-3-*C*-methyl-4-*O*-(*tert*-butyldimethylsilyl)-β-D-arabinopyranoside (33) and (2*S*,3*S*,4*S*,5*R*/*S*)-1,4-Di-*O*-acetyl-5-*O*-benzyl-3-methyl-2-*O*-(*tert*-butyldimethylsilyl)-1,2,4,5-hexanetetrol (34/35).** Benzyl 3-deoxy-3-*C*-methyl-4-*O*-(*tert*-butyldimethylsilyl)-α-D-arabinopyranoside (**11**) (64 mg, 182 μmol) was subjected to reaction conditions A (reflux, 18 h). Column chromatography (E/H, 1:6) gave **33** (44.4 mg, 69%) and a ring-opened diol, which was difficult to purify and therefore was acetylated. Column chromatography (E/H, 1:3) gave the diacetate **34/35** (22.1 mg, 27%, diastereomeric ratio >25:1). **33**: $[\alpha]^{20}_D$ = −160° (*c* 1.03, $CHCl_3$). The $^1H$ NMR spectrum of **33** was identical with the spectrum of compound **12** (enantiomer) (cf. ref 2, compound **21**). Anal. Calcd for $C_{19}H_{32}O_4Si$: C, 64.73; H, 9.15. Found: C, 64.75; H, 9.20.

**34/35**: $[\alpha]^{20}_D$ = −20.7° (*c* 0.96, $CHCl_3$); $^1H$ NMR δ 7.32 (m, 5 H, $C_6H_5$), 5.14 (dd, 1 H, $J_{3,4}$ = 4.3 Hz, H-3), 4.58, 4.51 (AB q, each 1 H, $J_{AB}$ = 11.7 Hz, $CH_2Ph$), 4.10, 3.98 (d, AB q, each 1 H, $J_{AB}$ = 11.4 Hz, $J_{1,2}$, $J_{1',2}$ = 3.7, 6.9 Hz, H-1, H-1'), 3.78 (m, 1 H, $J_{2,3}$ = 4.8 Hz, H-2), 3.66 (dq, 1 H, $J_{4,5}$ = 5.2 Hz, H-5), 2.14 (m, 1 H, H-4), 2.06, 2.02 (s, each 3 H, COMe), 1.18 (d, 3 H, $J_{5,6}$ = 6.4 Hz, H-6), 0.96 (d, 3 H, $J_{Me,3}$ = 7.1 Hz, 3-Me), 0.88 (s, 9 H, $Me_3CSi$), 0.06 (s, 6 H, $Me_2Si$). Anal. Calcd for $C_{24}H_{40}O_6Si$: C, 63.68; H, 8.91. Found: C, 63.51; H, 9.01.

**(2*S*,3*R*,4*S*,5*R*)- and (2*R*,3*R*,4*S*,5*S*)-1-*O*-Acetyl-3,5-di-*O*-isopropylidene-4-methyl-2-*O*-(*tert*-butyldimethylsilyl)-1,2,3,5-hexanetetrol (36 and 37).** Compound **13/14** (367 mg, 996 μmol) were partially acetylated (as described in General Methods except that 1.1 equiv of acetic anhydride was used.). Column chromatography (E/H, 1:5) gave the 1-*O*-acetates of **13/14**, which were hydrogenolyzed ($H_2$, Pd/C) in ethanol at room temperature for 24 h. The 3,5-diols thus obtained were dissolved in 5 mL of 2,2-dimethoxypropane, and a small amount of camphorsulfonic acid was added. Ater 25 min, the mixture was diluted with 5 mL of ethyl acetate, washed with saturated aqueous $NaHCO_3$ (3 mL) and water (3 mL), dried ($Na_2SO_4$), and concentrated. Column chromatography (E/H, 1:12) gave **36/37** (263 mg, 73% from **13/14**, ratio **36:37** = 10:1): $[\alpha]^{20}_D$ = −12.5° (*c* 0.89, $CHCl_3$); $^1H$ NMR δ 4.30, 3.97 (d AB q, each 1 H, $J_{AB}$ = 11.5 Hz, $J_{1,2}$, $J_{1',2}$ = 1.6 Hz, 5.3 Hz, H-1, H-1'), 4.08 (dq, 1 H, $J_{4,5}$ = 2.2 Hz, H-5), 3.84 (m, 1 H, $J_{2,3}$ = 9.1 Hz, H-2), 3.79 (dd, 1 H, $J_{3,4}$ = 1.9 Hz, H-3), 2.07 (s, 3 H, COMe), 1.60 (m, 1 H, H-4), 1.40, 1.36 (s, each 3 H, $Me_2C$), 1.14 (d, 3 H, $J_{5,6}$ = 6.4 Hz, H-6), 0.88 (d, 3 H, $J_{Me,4}$ = 6.4 Hz, 4-Me), 0.87 (s, 9 H, $Me_3CSi$), 0.10, 0.09 (2 s, each 3 H, $Me_2Si$). Anal. Calcd for $C_{18}H_{36}O_5Si$: C, 59.96; H, 10.06. Found: C, 60.14; H, 10.14.

**(2*R*,3*S*,4*R*,5*R*)- and (2*R*,3*S*,4*R*,5*S*)-1-*O*-Acetyl-3,5-di-*O*-isopropylidene-4-methyl-7-(trimethylsilyl)-2-*O*-(*tert*-butyldimethylsilyl)-1,2,3,5-heptanetetrol (38 and 39).** Compounds **19/20** (330 mg, 733 μmol) were partially acetylated (at the primary hydroxyl group), hydrogenated/hydrogenolyzed, and acetalized as described in the preparation of **36/37**. Column chromatography (E/H, 1:15) gave **38/39** (172 mg, 53% from **19/20**, ratio **38:39** > 20:1): $[\alpha]^{20}_D$ = −3.7° (*c* 0.92, $CHCl_3$); $^1H$ NMR δ 4.28, 4.02 (d AB q, each 1 H, $J_{AB}$ = 11.7 Hz, $J_{1,2}$, $J_{1',2}$ = 1.9, 5.0 Hz, H-1, H-1'), 3.88 (m, 1 H, $J_{2,3}$ = 9.3 Hz, H-2), 3.81 (dd, 1 H, $J_{3,4}$ = 4.2 Hz, H-3), 3.16 (q, 1 H, $J_{5,6}$ = 6.5 Hz, H-5), 2.07 (s, 3 H, COMe), 1.79 (m, 1 H, $J_{4,5}$ = 6.9 Hz, H-4), 1.50 (m, 2 H, H-6), 1.30, 1.30 (2 s, each 3 H, $Me_2C$), 0.94 (d, 3 H, $J_{Me,4}$ = 6.8 Hz, 4-Me), 0.87 (s, 9 H, $Me_3CSi$), 0.70, 0.41 (AB q complex, each 1 H, H-7), 0.10, 0.08 (2 s, each 3 H, $Me_2Si$), 0.00 (s, 9 H, $Me_3Si$). Anal. Calcd for $C_{22}H_{46}O_5Si_2$: C, 59.14; H, 10.38. Found: C, 59.08; H, 10.70.

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**Supplementary Material Available:** Discussion about the structure determination of **36/37** and **38/39**; Scheme IV and Figure 1 showing the calculated (MM2(85)) low-energy conformers of model acetonides **36'–39'**; Table 2 listing calculated (3JHH) and experimental NMR coupling constant data for **36'–39'**, **36**, and **38**; Figure 2 showing selected NOE data for acetonides **36** and **38**; Experimental Section describing the preparation of 6-(3OTBS) (4 pages). Ordering information is given on any current masthead page.