

P, and Si radicals) the values are clustered above 5 G. The only anomalous carbon-centered radical adduct is the very polar cyanyl species with its  $\alpha$ - $^{13}\text{C}$  HFS value of 3.40 G, which is consistent with the pseudohalide nature of this substituent.

It is also possible to plot the N HFS's of  $\alpha$ -substituted aminoxy radicals from various radical adducts for two different spin traps, DMPO and PBN. These plots in benzene and water are shown in Figure 8. Despite the considerable differences in the parent structures of these radical adducts, both the benzene and water plots exhibited significant linear character. These results suggest that the

N HFS's of radical adducts of PBN or DMPO may themselves serve as viable substituent scales ( $\sigma_{\text{RA}}$ ) for the determination of the substructures of other  $\alpha$ -substituted aminoxy radicals. Spectral correlations of this type between the radical adducts<sup>24</sup> of PBN and DMPO analogues or C-nitroso compounds may also prove to be useful.

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## Regioselective and Stereoselective Oxirane Ring-Openings of 2,3-Anhydropentopyranosides with Some Methyl Group Donating Organometallic Reagents

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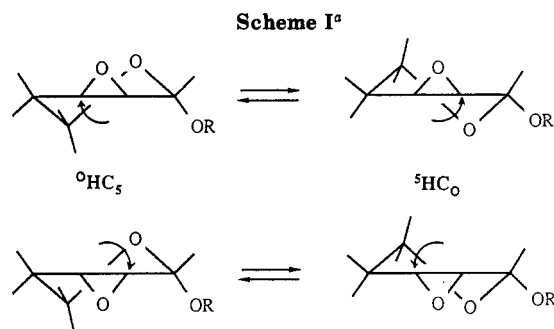
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By the proper choice of methyl group transferring organometallic reagents ( $\text{Me}_4\text{AlLi}$ ,  $\text{Me}_4\text{AlLi/MeLi}$  (1:1),  $\text{Me}_2\text{CuLi}$ ,  $\text{Me}_3\text{Al}$ ,  $\text{Me}_2\text{Mg}$ ) it is possible to selectively introduce a methyl group into the 2- or 3-position via epoxide ring-opening of four easily available benzyl 2,3-anhydro-4-*O*-(*tert*-butyldimethylsilyl)pentopyranosides (2, 6, 8, 12). The resulting 2-deoxy-2-*C*-methyl- and 3-deoxy-3-*C*-methylglycosides (14-21) were obtained in 84-35% yield and may be useful as chiral starting materials in organic synthesis.

In connection with work on the total synthesis of natural products, we required access to suitably protected 2-deoxy-2-*C*-methylpentopyranosides. As far as we know, no efficient method for the preparation of these potentially valuable chiral synthons<sup>1</sup> has hitherto been described. It has been reported that catalytic hydrogenation of 2-*C*-methylenepentoses gave moderate yields of 2-deoxy-2-*C*-methyl sugars.<sup>2,3</sup> However, the stereoselectivity was low and the diastereomers were not easily separated. A more convenient approach would be to introduce the methyl group via a regio- and stereoselective oxirane ring-opening.

The nucleophilic opening of conformationally rigid 2,3-anhydropentopyranosides, notably the 4,6-di-*O*-benzylidene and 1,6-anhydro sugars, predominantly yields the *trans*-diaxial products, in accordance with the Fürst-Plattner rule.<sup>4,5</sup> Among the carbon nucleophiles, organocuprates, dialkylmagnesiums, and functionalized alkylnylalanes have proven effective.<sup>6</sup> Organolithiums as well as Grignard reagents, with the exception of allylmagnesium halides,<sup>7</sup> lead to considerable amounts of various reduction



<sup>a</sup> Curved arrows indicate the preferential site of attack by a nucleophile according to the Fürst-Plattner rule.

and elimination products, as well as to halohydrins.<sup>8</sup>

Due to the ease of interconversion between the two half-chair forms of 2,3-anhydropentopyranosides (Scheme I), the regiochemistry of their opening is likely to be more sensitive to steric and coordinative properties of the reagent, as compared to the hexoses, and lack of selectivity is often found.<sup>4,9</sup> In the few cases reported of carbon nucleophiles, i.e., with various organolithiums,<sup>10</sup> cyanide,<sup>11</sup>

(1) For a recent review, see: Inch, T. D. *Tetrahedron* 1984, 40, 3161. Examples are also found in: Hanessian, S. *Total Synthesis of Natural Products: The Chiron Approach*, Pergamon: New York, 1983.

(2) Rosenthal, A.; Sprinzl, M. *Can. J. Chem.* 1970, 48, 3253.

(3) Depeyaz, J. C.; LeMerrer, Y. *Carbohydr. Res.* 1980, 83, 51.

(4) For a review, see: Williams, N. R. *Adv. Carbohydr. Chem. Biochem.* 1970, 25, 109.

(5) Grindley, T. B.; Reimer, G. J.; Kralovec, J.; Brown, R. G.; Anderson, M. *Can. J. Chem.* 1987, 65, 1065.

(6) For examples, see: (a) Fraser-Reid, B.; Magdzinski, L.; Molino, B.; Mootoo, D. R. *J. Org. Chem.* 1987, 52, 4495. (b) Parker, K. A.; Babine, R. E. *Tetrahedron Lett.* 1982, 23, 1763. (c) Kochetkov, N. K.; Sviridov, A. F.; Ermolenko, M. S. *Tetrahedron Lett.* 1981, 22, 4315. (d) Hicks, D. R.; Fraser-Reid, B. *Can. J. Chem.* 1975, 53, 2017.

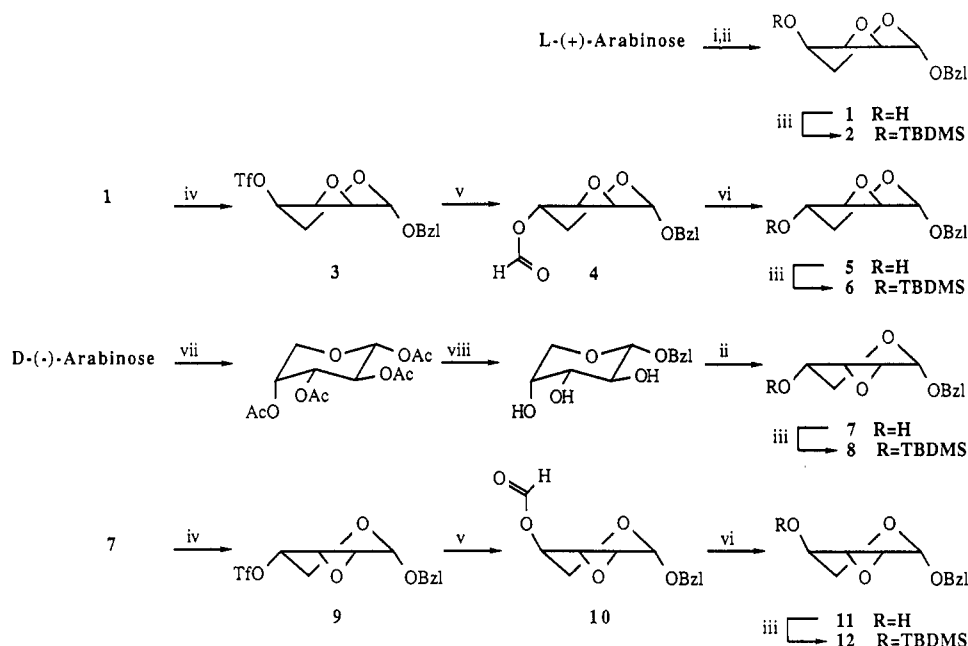
(7) (a) Sunay, U.; Fraser-Reid, B. *Tetrahedron Lett.* 1986, 27, 5335. (b) Challenger, S.; Procter, G. *Tetrahedron Lett.* 1986, 27, 391.

(8) Inch, T. D.; Lewis, G. J. *Carbohydr. Res.* 1970, 15, 1.

(9) See, for example: (a) Janairo, G.; Kowolik, W.; Voelter, W. *Liebigs Ann. Chem.* 1987, 165. (b) Afza, N.; Malik, A.; Voelter, W. *J. Chem. Soc., Perkin Trans. 1* 1983, 1349. (c) Paulsen, H.; Patt, H. *Liebigs Ann. Chem.* 1981, 1633. (d) Dwivedi, S. K.; Khare, A.; Khare, M. P. *Carbohydr. Res.* 1981, 91, 159. (e) Lemieux, R. U.; Watanabe, K. A.; Pavia, A. A. *Can. J. Chem.* 1969, 47, 4413.

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(11) (a) Davison, B. E.; Guthrie, R. D. *J. Chem. Soc., Perkin Trans. 1* 1972, 658. (b) Williams, N. R. *J. Chem. Soc., Chem. Commun.* 1967, 1012.

Scheme II<sup>a</sup>

<sup>a</sup> (i) BzOH, HCl. (ii) Acetone, triethyl orthoformate, H<sup>+</sup>; TsCl, pyridine; EtOH/H<sub>2</sub>O, H<sup>+</sup>; NaOMe, MeOH. (iii) TBDMSCl, imidazole, DMF. (iv) (TfO)<sub>2</sub>O, pyridine, CH<sub>2</sub>Cl<sub>2</sub>. (v) DMF/H<sub>2</sub>O. (vi) NaOH, DMF/H<sub>2</sub>O. (vii) Ac<sub>2</sub>O, NaOAc. (viii) BzOH, BF<sub>3</sub>·OEt<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, followed by NaOMe, MeOH.

and dimethylmagnesium,<sup>12</sup> no significant C-2 substitution has been substantiated.

We now report an investigation of the oxirane ring-opening of four diastereomeric 2,3-anhydropentopyranosides with some methyl group donating reagents.

## Results and Discussion

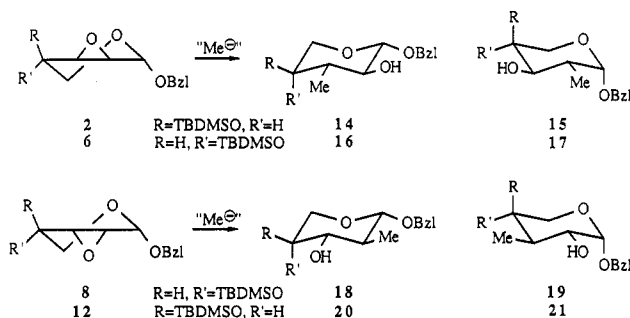
The oxiranes investigated in this work (2, 6, 8, 12) were prepared according to Scheme II. The known ribosides 1<sup>13</sup> and 7,<sup>14</sup> synthesized on a multigram scale from commercially available L-(+)- and D-(-)-arabinose, were converted to the stable, crystalline triflates 3 and 9.<sup>15,16</sup> We observed that by dissolving 3 or 9 in DMF containing 0.1–2% of water, the formates 4 or 10 were formed in 89% yield after a few minutes.<sup>17</sup> The formates (either isolated or in situ) were hydrolyzed with aqueous sodium hydroxide in DMF, to yield oxirane 5 (previously synthesized by other less efficient routes<sup>9c,15,18</sup>) and the novel oxirane 11, respectively. The epoxy sugars 1, 5, 7, and 11 were conventionally silylated<sup>19</sup> to give the 4-*O*-*tert*-butyldimethylsilyl (TBDMS) pyranosides 2, 6, 8, and 12, in high yields.

Table I. Selected <sup>1</sup>H NMR Coupling Constants

compd	coupling constants, Hz			
	<i>J</i> <sub>1,2</sub>	<i>J</i> <sub>2,3</sub>	<i>J</i> <sub>3,4</sub>	<i>J</i> <sub>4,5</sub> , <i>J</i> <sub>4,5'</sub>
2	<0.2	3.8	3.3	5.0, 6.0
6	<0.2	3.8	0.7	7.3, 9.3
8	3.2	4.1	1.7	5.7, 10.2
12	2.8	3.9	1.8	2.8, 2.8
14	6.0	8.5	8.1	3.9, 8.0
15	3.4	<i>a</i>	<i>a</i>	<i>a</i>
3-OAc of 15	3.3	11.2	2.9	0.8, 2.6
16	7.0	10.3	3.2	1.4, 2.3
17	3.5	<i>a</i>	<i>a</i>	<i>a</i>
3-OAc of 17	3.4	11.2	8.1	<i>a</i>
18	4.4	7.3	3.4	2.9, 5.8
19	3.9	10.8	<i>a</i>	<i>a</i>
2-OAc of 19	3.4	11.6	9.4	5.1, 10.5
20	7.7	9.6	7.8	4.8, 9.2
21	3.7	11.2	2.6	1.2, 2.0

<sup>a</sup> Unresolved.

## Scheme III



Due to differences in the physical data of our preparation of 5 and 11 and those reported,<sup>17b</sup> we decided to establish their structures unequivocally. In the basic hydrolysis of 4 and 10 there was the risk of Payne rearrangement,<sup>20</sup> which would give the 3,4-anhydroglycosides

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(15) Kimmich, R.; Voelter, W. *Liebigs Ann. Chem.* 1981, 1100.

(16) For a review on carbohydrate triflates, see: Binkley, R. W.; Ambrose, M. G. *J. Carbohydr. Chem.* 1984, 3, 1.

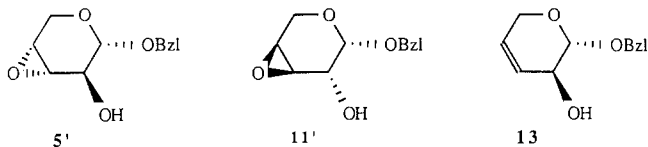
(17) (a) During our work it was reported that the formate 4 was formed in 30% yield when 3 was treated with CsF in DMF during 3 h at room temperature: Latif, F.; Malik, A.; Voelter, W. *Liebigs Ann. Chem.* 1987, 617. (b) Compounds 3 and 9 have been reported to undergo C-4 inversion upon treatment with tetrabutylammonium nitrate (or pyridine) in aqueous dimethylformamide (DMF) to give 5 and 11: Kowolik, W.; Malik, A.; Afza, N.; Voelter, W. *J. Org. Chem.* 1985, 50, 3325. The data reported for 5 and 11 were, however, not in accordance with our data or, in the case of 5, with the data reported by others (cf. ref 9c, 15, and 18).

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(19) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* 1972, 94, 6190.

(20) (a) Payne, G. B. *J. Org. Chem.* 1962, 27, 3819. (b) Buchanan, J. G.; Fletcher, R. *J. Chem. Soc. C* 1966, 1926.

5' and 11', respectively. This could be ruled out since



there exists convincing physical and spectral literature data for 5'<sup>18</sup> as well as for the methylglycosides corresponding to 5' and 11'.<sup>21</sup> Due to the small coupling constants, long-range couplings, and closely positioned signals in the NMR spectra of 5 and 11 (see Experimental Section), it was difficult to make the complete proton signal assignment on the basis of routine NMR experiments (including double resonance). The proton connectivities were instead obtained from COSY experiments on their 4-*O*-TBDMS derivatives 6 and 12, which support the structural assignments of 5 and 11. Since the conformations of the substrates in the present investigation (2, 6, 8, and 12) seem to be important in terms of the selectivity of the oxirane ring-opening, it should be mentioned that their H-4-H-5 and H-4-H-5' proton coupling constants (Table I) indicate a preference for the <sup>0</sup>HC<sub>5</sub> conformation (Scheme I), in agreement with other investigations.<sup>21</sup>

The results of the oxirane ring-opening reactions of 2, 6, 8, and 12, leading to 2-deoxy-2-*C*-methyl- and 3-deoxy-3-*C*-methylpyranosides 14–21 (Scheme III), are shown in Table II.

It is well-known that lithium dimethylcuprate (Me<sub>2</sub>CuLi) attacks oxiranes with inversion at the sterically least hindered carbon.<sup>22</sup> Comparison of anhydro sugars 2 and 6 (entries 1 and 5), both anticipated to yield the 3-deoxy-3-*C*-methyl products according to the Fürst-Plattner (Scheme I), shows that the bulky TBDMSO group affects the regiochemical result of their reactions with Me<sub>2</sub>CuLi. Only attack on C-3 was observed with 2 as expected, but the principal product of this reaction was the allylic alcohol 13, formed via a reductive elimination of 2 (cf. ref 5 and 23). The opening of 6, on the other hand, gave the unexpected 2-deoxy-2-*C*-methyl product 17. A plausible explanation for this result is that the reaction took place with the less stable <sup>5</sup>HC<sub>0</sub> conformer (Scheme I), which would give the observed product according to the Fürst-Plattner rule. Also, due to the stereoelectronic effect in the acetal function of 6, the benzyl group should be oriented anti to C-2,<sup>24</sup> which would leave this position relatively open for attack. The reaction time and temperature were more forcing with 6 than with 2 in order to consume the starting materials. It is thus possible that the reactivity of the 3-position of the <sup>0</sup>HC<sub>5</sub> conformation of 6 is low due to steric hindrance from the TBDMSO group, which gives the thermodynamically less favored <sup>5</sup>HC<sub>0</sub> conformation a chance to compete, resulting in C-2 attack of the reagent.

Compound 8, with the epoxide ring cis to both substituents, reacted rapidly with Me<sub>2</sub>CuLi, but the two positions were attacked at comparable rates. Lowering of the temperature, as well as use of excess reagent, did not markedly affect the regioselectivity, while inversion of the stereochemistry at the 4-position, i.e., with 12 as the substrate, effectively hindered C-3 attack (cf. entries 10 and 15). The use of lithium dimethylcyanocuprate<sup>25</sup> generally

required prolonged reaction times with these substrates and was not advantageous with respect to yield or regioselectivity (results not shown).<sup>26</sup>

A reaction pattern similar to that of Me<sub>2</sub>CuLi emerged with lithium tetramethylaluminum (Me<sub>4</sub>AlLi),<sup>27</sup> a reagent previously not applied to carbohydrate epoxides. Good yields and complete regioselectivity were found in the reactions of 2 and 12 (entries 2 and 16). The results of the opening of 8 (entry 11) led us to conduct a series of experiments to establish the influence of the solvent composition and of the reagent stoichiometry on the reaction. In a noncoordinating solvent, such as hexane, Me<sub>4</sub>AlLi is probably associated with the oxirane, which may enhance its reactivity, whereas in the presence of diethyl ether the reagent is less reactive, probably due to complexation with the solvent.<sup>28</sup> In the reactions with 8, the rate was indeed reduced with increasing diethyl ether content (from ~0–80%) in hexane and, furthermore, the C-2/C-3 ratio increased (from 0.5 to 1.0). Since Me<sub>4</sub>AlLi was prepared by mixing methyl lithium (MeLi) with trimethylaluminum (Me<sub>3</sub>Al), the relative stoichiometric amounts of MeLi, Me<sub>3</sub>Al, and Me<sub>4</sub>AlLi could be easily varied. Thus, by increasing the amount of MeLi from 0.75 to 2.0 equiv with respect to Me<sub>3</sub>Al, the C-2/C-3 ratio increased from 0.75 to 4.5, while MeLi alone reacted very slowly and gave only traces of products (data not shown). The best reaction conditions with respect to C-2 substitution are those given in entry 12.

These experiments clearly indicated that the stoichiometric composition of the reagent mixture was of importance for both the rate and the regiochemistry of the reaction. The low reactivity of MeLi made it doubtful that it (as a species per se) took part in the reactions, but the results of the opening of 6 showed that MeLi may actually do so. When the stoichiometry of MeLi and Me<sub>3</sub>Al was 1:1 (i.e., Me<sub>4</sub>AlLi should be present as the major species), only traces of 16 and 17 were formed (entry 6). On the other hand, when the stoichiometry was 2:1 (i.e., a 1:1 mixture of Me<sub>4</sub>AlLi and MeLi should be present), the yield of 17 was 84% but 16 was not found. <sup>7</sup>Li NMR data of Me<sub>4</sub>AlLi/MeLi mixtures have been interpreted as resulting from the dissociation of the tetrameric MeLi to the dimeric form.<sup>29</sup> This finding may offer part of an explanation of our results, since it seems reasonable that the dimeric form of MeLi is more reactive than the tetrameric one.<sup>30</sup> Further experimentation will, however, be required in order to establish whether this is a common effect in oxirane openings with this reagent combination.

Me<sub>3</sub>Al is a Lewis acid known to form stable complexes with ethers and other Lewis bases.<sup>27</sup> In the cleavage of epoxides, in noncoordinating solvents, the epoxide-alane complex is attacked at the highest substituted carbon, usually with inversion.<sup>31</sup> Since the electron-withdrawing

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(27) For reviews on organoaluminum chemistry, see: (a) Negishi, E.-I. *Organometallics in Organic Chemistry*; Wiley-Interscience: 1980; Vol. I. (b) Mole, T.; Jeffery, E. A. *Organoaluminum Compounds*; Elsevier: New York 1972.

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Table II. Results of the Ring-Opening of Epoxides 2, 6, 8, and 12 with Various Methyl Group Transferring Reagents

entry	epox	reagent	equiv	temp, °C; time, h	solvent	product, % yield <sup>a</sup>	
						2-C-Me	3-C-Me
1	2	Me <sub>2</sub> CuLi	2.0	0; 2	ether	15, ~0 <sup>b</sup>	14, 30
2	2	Me <sub>4</sub> AlLi	1.1	reflux; 24	hexane/ether	15, ~0	14, 82 (80)
3	2	Me <sub>3</sub> Al	1.3	reflux; 27	hexane	15, 37 (35)	14, 11 (10)
4	2	Me <sub>2</sub> Mg	20	reflux; 48	ether	15, 9	14, 12
5	6	Me <sub>2</sub> CuLi	5.0	20; 30	ether	17, 70 (69)	16, ~0
6	6	Me <sub>4</sub> AlLi	1.1	reflux; 5	hexane/ether	17, c	16, c
7	6	Me <sub>4</sub> AlLi/MeLi <sup>d</sup>	1.1:1.1	20; 3.5	hexane/ether	17, 84 (84)	16, ~0
8	6	Me <sub>3</sub> Al	1.3	reflux; 24	hexane	17, ~2	16, 56 (54)
9	6	Me <sub>2</sub> Mg	20	reflux; 69	ether	17, 8	16, 80 (80)
10	8	Me <sub>2</sub> CuLi	1.1	0; 0.6	ether	18, 38	19, 43
11	8	Me <sub>4</sub> AlLi	1.1	reflux; 5	hexane/ether	18, 48	19, 48
12	8	Me <sub>4</sub> AlLi/MeLi <sup>d</sup>	1.1:1.1	reflux; 0.8	hexane/ether	18, 67 (66)	19, 15 (14)
13	8	Me <sub>3</sub> Al	4.0	reflux; 45	hexane	18, ~0	19, 38 (38)
14	8	Me <sub>2</sub> Mg	2.0	reflux; 24	ether	18, ~3	19, 13
15	12	Me <sub>2</sub> CuLi	3.0	0; 3	ether	20, 76 (73) <sup>e</sup>	21, ~2
16	12	Me <sub>4</sub> AlLi	1.1	reflux; 4	hexane/ether	20, 88 (80) <sup>e</sup>	21, ~0
17	12	Me <sub>3</sub> Al	2.6	reflux; 48	hexane	20, ~3	21, 49 (47)
18	12	Me <sub>2</sub> Mg	20	reflux; 66	ether	20, 52	21, 28

<sup>a</sup> Yields determined by HPLC analysis of the crude product. Isolated yields are shown in parentheses. Less than 5% of unreacted epoxide was found except in entries 5 (9%) and 14 (14%). <sup>b</sup> Benzyl β-L-glycero-pent-3-enopyranoside (13) was isolated in 68% yield. <sup>c</sup> Complex product mixture. Only traces of 16 and 17 were formed. <sup>d</sup> By the use of MeLi (2.2 equiv) instead of Me<sub>4</sub>AlLi/MeLi, only traces of products were formed. <sup>e</sup> Isolated as the 3-O-acetate.

character of the anomeric carbon is likely to destabilize a developing positive charge at C<sub>2</sub>, C<sub>3</sub> attack is anticipated to dominate, and with the exception of 2, this turned out to be the case (entries 3, 8, 13, and 17). We have, however, observed that the primary products (i.e., the C-2(3)-methyl C-3(2)-alcoholates) underwent subsequent reactions with Me<sub>3</sub>Al to give as yet unknown compounds. This makes it difficult to interpret the results in terms of regioselectivity, since the isomers may react further at different rates.

The reactions with dimethylmagnesium (Me<sub>2</sub>Mg)<sup>32</sup> in diethyl ether appear to be sensitive to obstruction of the complex formation between the reagent and the epoxide oxygen, since the good yields obtained with 6 and 12, both having the oxirane ring trans to the TBDMSO group, were not repeated with the more hindered 2 and 8. Instead, a mixture of products was obtained with low yields of the desired ones (cf. entries 9, 18 and 4, 14).

The structures of the eight isomeric deoxy-C-methylpyranosides 14–21 were determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. From the magnitude of the proton coupling constants (Table I) it appears as if the favored conformations of 14–17 and 19–21 are those with equatorial C-2 and C-3 substituents (as depicted in Scheme III). In the case of 18, however, the coupling constants are intermediary, possibly due to an equilibrium between the <sup>4</sup>C<sub>1</sub> and <sup>1</sup>C<sub>4</sub> chair forms.

### Conclusions

We have shown that by the proper choice of reagent a methyl group may be introduced preferentially at either C-2 or C-3 of the 2,3-anhydropentopyranoside derivatives 2, 6, 8, and 12, which makes the products 14–21 available for use as chiral building units in organic synthesis.

The rate and regiochemistry of the oxirane openings are mainly determined by the steric demands of the nucleophilic ate-complexes, Me<sub>2</sub>CuLi and Me<sub>4</sub>AlLi, in the presence of diethyl ether. The sterically least hindered carbon of the oxirane ring is preferentially attacked. With the Lewis acidic reagents, Me<sub>3</sub>Al and Me<sub>2</sub>Mg, C-3 substitution

is generally observed. However, the forcing reaction conditions necessary to consume the oxiranes in some cases result in low total yields of the deoxy methyl compounds due to side reactions.

### Experimental Section

Column chromatography separations were performed by using Merck SiO<sub>2</sub> 60 (0.040–0.063 mm) silica gel, with ethyl acetate/heptane (E/H) mixtures as eluents. TLC analyses were done on Merck SiO<sub>2</sub> 60 F254 precoated glass plates, and the spots were visualized by charring with 10% aqueous H<sub>2</sub>SO<sub>4</sub>. Melting points were determined with a Reichert microscope and are uncorrected. NMR spectra were recorded at 23 °C with a Varian XL-300 spectrometer (software version 6.2) using CDCl<sub>3</sub> as solvent and CHCl<sub>3</sub> as internal standard (δ 7.26 compared to TMS). HPLC analyses were performed by using a 250 × 4 mm column packed with Merck LiChrosorb Si100 (5 μm), an LKB 2150 pump, and a Varian RI-3 refractive index detector. Optical rotations were measured with a Perkin-Elmer 141 polarimeter. IR spectra were recorded on a Perkin-Elmer 257 spectrometer. MeLi (~1.6 M in diethyl ether) was purchased from Fluka AG and was titrated before use. Trimethylaluminum (2.0 M in hexanes) and Me<sub>2</sub>Mg (0.64 M in diethyl ether) were purchased from Aldrich and Alfa-Ventron, respectively. Benzyl 2,3-anhydro-β-L-ribofuranoside (1) was prepared from L-(+)-arabinose in 60% yield.<sup>13</sup> 1,2,3,4-Tetra-O-acetyl-α-D-arabinopyranose was prepared from D-(–)-arabinose in 56% yield.<sup>33</sup>

**Benzyl 2,3-Anhydro-4-O-(tert-butyltrimethylsilyl)-β-L-ribofuranoside (2).** tert-Butyltrimethylsilyl chloride (4.07 g, 27.0 mmol) and imidazole (3.83 g, 56.2 mmol) were dissolved in DMF (15 mL, dried over 4-Å molecular sieves). The solution was heated to 35 °C, and then 1 (5.00 g, 22.5 mmol) was added in portions. After 50 min, dichloromethane (15 mL) was added and the solution was washed with aqueous HCl (1 M, 30 mL), saturated aqueous NaHCO<sub>3</sub> (30 mL), and water (30 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated in vacuo. Column chromatography (E/H, 1:15) of the residue gave 2 (syrup, 7.34 g, 98%): [α]<sub>D</sub><sup>20</sup> +13° (c 0.99, CHCl<sub>3</sub>); <sup>1</sup>H NMR δ 7.34 (m, 5 H, C<sub>6</sub>H<sub>5</sub>), 4.96 (s, 1 H, H-1), 4.83, 4.58 (AB q, each 1 H, J<sub>AB</sub> = 11.6 Hz, CH<sub>2</sub>Ph), 4.16 (dq, 1 H, J<sub>3,4</sub> = 3.3 Hz, H-4), 3.71, 3.33 (d AB q, each 1 H, J<sub>AB</sub> = 11.6 Hz, J<sub>4,5</sub>, J<sub>4,5'</sub> = 5.0 Hz, 6.0 Hz, H-5, H-5'), 3.35 (t, 1 H, J<sub>2,3</sub> = 3.8 Hz, H-3), 3.28 (d, 1 H, H-2), 0.92 (s, 9 H, Me<sub>3</sub>CSi), 0.14, 0.12 (2 s, each 3 H, Me<sub>2</sub>Si); <sup>13</sup>C NMR δ 136.9 (PhC), 128.4, 128.0, 127.9 (PhCH), 94.8 (C-1), 70.6 (CH<sub>2</sub>Ph), 64.8, 61.6, 54.3, 53.1 (C-2, C-3, C-4, C-5), 25.9 (Me<sub>3</sub>CSi), 18.3 (Me<sub>2</sub>CSi), -4.5, -4.6 (Me<sub>2</sub>Si).

(32) For a comparison of Me<sub>2</sub>Mg and Me<sub>3</sub>Al in reactions with various oxiranes, see: Boireau, G.; Abenhaim, D.; Namy, J. L.; Henry-Basch, E. *Zh. Org. Khim.* 1976, 12, 184.

(33) Kuszmann, J.; Vargha, L. *Rev. Chim., Acad. Repub. Pop. Roum.* 1962, 7, 1025.

Anal. Calcd for  $C_{15}H_{28}O_4Si$ : C, 64.24; H, 8.39. Found: C, 64.19; H, 8.40.

**Benzyl 2,3-Anhydro-4-O-formyl- $\alpha$ -D-lyxopyranoside (4).** Benzyl 2,3-anhydro-4-O-[(trifluoromethyl)sulfonyl]- $\beta$ -L-ribo-pyranoside (3, 708 mg, 2.00 mmol; prepared from 1 in 91% yield<sup>15</sup>) was dissolved in DMF (15 mL, containing 2% of water). After the mixture was stirred at room temperature for 45 min, dichloromethane (50 mL) was added, and the solution was washed with aqueous HCl (0.1 M, 30 mL), saturated aqueous  $NaHCO_3$  (15 mL), and water. The organic phase was dried ( $Na_2SO_4$ ) and concentrated in vacuo. Column chromatography (E/H, 1:5) of the residue gave 4 (445 mg, 89%): mp 66.5–67.0 °C;  $[\alpha]_D^{20} +73.7^\circ$  (c 1.01,  $CHCl_3$ );  $^1H$  NMR  $\delta$  8.09 (m, 1 H, CHO), 7.37 (m, 5 H,  $C_6H_5$ ), 5.11 (m, 1 H, H-4), 5.02 (d, 1 H,  $J_{1,2} = 0.6$  Hz, H-1), 4.83, 4.60 (AB q, each 1 H,  $J_{A,B} = 11.6$  Hz,  $CH_2Ph$ ), 3.73, 3.63 (d AB q, each 1 H,  $J_{A,B} = 11.5$  Hz,  $J_{4,5}, J_{4,5'} = 6.0$  Hz, 8.5 Hz, H-5, H-5'), 3.33 (m, 1 H,  $J_{2,3} = 3.5$  Hz, H-3), 3.20 (m, 1 H, H-2);  $^{13}C$  NMR  $\delta$  159.5 (CHO), 136.8 (PhC), 128.5, 128.1 (PhCH), 94.1 (C-1), 70.3 ( $CH_2Ph$ ), 63.2, 57.1, 52.3, 50.3 (C-2, C-3, C-4, C-5); IR (KBr) 1717 (C=O), 1190, 1030  $cm^{-1}$ .

Anal. Calcd for  $C_{13}H_{14}O_5$ : C, 62.39; H, 5.64. Found: C, 62.40; H, 5.61.

**Benzyl 2,3-Anhydro- $\alpha$ -D-lyxopyranoside (5).** Compound 3 (9.00 g, 25.4 mmol) was dissolved in DMF (250 mL, containing 0.1% water). After the mixture was stirred at room temperature for 30 min, aqueous NaOH (1.0 M, 38 mL) was added dropwise over a period of 45 min. After 1 h, the solution was neutralized with aqueous HCl (2 M), concentrated (0.5 mmHg), and dissolved in  $CH_2Cl_2$  (300 mL). The organic solution was washed with  $NaHCO_3$  (2%, 75 mL) and water (75 mL), dried ( $Na_2SO_4$ ), and concentrated in vacuo. Column chromatography (E/H, 1:3) of the residue gave 5 (4.41 g, 78%), which was recrystallized from ethyl acetate/hexane: mp 63.5–64.5 °C;  $[\alpha]_D^{20} +105^\circ$  (c 1.02,  $CHCl_3$ );  $^1H$  NMR  $\delta$  7.37 (m, 5 H,  $C_6H_5$ ), 4.98 (s, 1 H, H-1), 4.85, 4.60 (AB q, each 1 H,  $J_{A,B} = 11.6$  Hz,  $CH_2Ph$ ), 4.02 (m, 1 H, H-4), 3.67, 3.57 (d AB q, each 1 H,  $J_{A,B} = 11.6$  Hz,  $J_{4,5}, J_{4,5'} = 6.9$  Hz, 5.0 Hz, H-5, H-5'), 3.32 (m, 1 H, H-3), 3.19 (d, 1 H,  $J_{2,3} = 3.8$  Hz, H-2), 1.8 (br s, 1 H, OH).

Anal. Calcd for  $C_{12}H_{14}O_4$ : C, 64.85; H, 6.35. Found: C, 64.83; H, 6.40.

**Benzyl 2,3-Anhydro-4-O-(tert-butylidimethylsilyl)- $\alpha$ -D-lyxopyranoside (6).** Compound 5 (3.30 g, 14.9 mmol) was silylated as described in the preparation of 2. Column chromatography (E/H, 1:35) yielded 6 (4.65 g, 93%): mp 33–35 °C;  $[\alpha]_D^{20} +79^\circ$  (c 0.98,  $CHCl_3$ );  $^1H$  NMR  $\delta$  7.37 (m, 5 H,  $C_6H_5$ ), 5.00 (s, 1 H, H-1), 4.80, 4.56 (AB q, each 1 H,  $J_{A,B} = 11.6$  Hz,  $CH_2Ph$ ), 3.94 (dq, 1 H,  $J_{4,5} = 9.3$  Hz,  $J_{4,5'} = 7.3$  Hz, H-4), 3.50, 3.48 (AB q, each 1 H,  $J_{A,B} = 12.6$  Hz, H-5, H-5'), 3.24 (d, 1 H,  $J_{2,3} = 3.8$  Hz, H-2), 3.12 (dd, 1 H,  $J_{3,4} = 0.7$  Hz, H-3), 0.91 (s, 9 H,  $Me_3CSi$ ), 0.13, 0.10 (2 s, each 3 H,  $Me_2Si$ );  $^{13}C$  NMR  $\delta$  137.1 (PhC), 128.4, 128.0, 127.9 (PhCH), 93.8 (C-1), 69.8 ( $CH_2Ph$ ), 62.6, 60.0, 56.5, 50.1 (C-2, C-3, C-4, C-5), 25.8 ( $Me_3CSi$ ), 18.1 ( $Me_3CSi$ ), -4.7, -4.8 ( $Me_2Si$ ).

Anal. Calcd for  $C_{18}H_{28}O_4Si$ : C, 64.24; H, 8.39. Found: C, 64.20; H, 8.38.

**Benzyl  $\alpha$ -D-Arabinopyranoside.** 1,2,3,4-Tetra-O-acetyl- $\alpha$ -D-arabinopyranose (100 g, 0.314 mol) was dissolved in  $CH_2Cl_2$  (1.0 L, dried over 4-Å molecular sieves), and then benzyl alcohol (98 mL, 0.94 mol) was added. After cooling of the reaction mixture to 0 °C,  $BF_3 \cdot OEt_2$ <sup>34</sup> (200 mL, 1.57 mol) was added during 5 min under a nitrogen atmosphere. The ice bath was removed, and after 1 h, the reaction mixture was poured into 1 L of ice water. The organic layer was separated, and the aqueous phase was extracted with  $CH_2Cl_2$  (300 mL). The combined organic phases were washed with saturated aqueous  $NaHCO_3$  (500 mL) and water (500 mL) and dried ( $Na_2SO_4$ ). The solvent was removed in vacuo, and then the crude product was deacetylated with a catalytic amount of sodium methoxide (2 mM) in methanol (800 mL). The base was neutralized by adding dry ion-exchange resin (Duolite-H<sup>+</sup>) to the reaction mixture. The solvent was removed in vacuo, and the residue was recrystallized from ethanol to give the title compound (54 g, 72%): mp 138.5–139.5 °C (lit.<sup>35</sup> mp 138–140

°C);  $[\alpha]_D^{20} +44.2^\circ$  (c 1.24, EtOH) (lit.<sup>35</sup>  $[\alpha]_D^{25} +49.8^\circ$  (c 1.0, EtOH)).

**Benzyl 2,3-anhydro- $\alpha$ -D-ribo-pyranoside (7)** was prepared in 73% overall yield from benzyl  $\alpha$ -D-arabinopyranoside according to ref 14: mp 96–97 °C;  $[\alpha]_D^{20} +134^\circ$  (c 0.98, EtOAc) (lit.<sup>14</sup> mp 94–96 °C;  $[\alpha]_D^{20} +202^\circ$  (c 1.0, EtOAc)).<sup>36</sup>

Anal. Calcd for  $C_{12}H_{14}O_4$ : C, 64.85; H, 6.35. Found: C, 64.8; H, 6.35.

**Benzyl 2,3-Anhydro-4-O-(tert-butylidimethylsilyl)- $\alpha$ -D-ribo-pyranoside (8).** Compound 7 (10.0 g, 45.0 mmol) was silylated as described in the preparation of 2. The crude product was recrystallized from hexane to give 8 (14.8 g, 98%): mp 61–62 °C;  $[\alpha]_D^{20} +131^\circ$  (c 0.84,  $CHCl_3$ );  $^1H$  NMR  $\delta$  7.35 (m, 5 H,  $C_6H_5$ ), 4.92 (d, 1 H,  $J_{1,2} = 3.2$  Hz, H-1), 4.79, 4.58 (AB q, each 1 H,  $J_{A,B} = 12.2$  Hz,  $CH_2Ph$ ), 4.10 (m, 1 H,  $J_{3,4} = 1.7$  Hz, H-4), 3.68, 3.34 (d AB q, each 1 H,  $J_{A,B} = 11.0$  Hz,  $J_{4,5}, J_{4,5'} = 10.2$  Hz, 5.7 Hz, H-5, H-5'), 3.42 (dd, 1 H,  $J_{2,3} = 4.1$  Hz, H-2), 3.31 (m, 1 H, H-3), 0.90 (s, 9 H,  $Me_3CSi$ ), 0.13, 0.10 (2 s, each 3 H,  $Me_2Si$ );  $^{13}C$  NMR  $\delta$  137.3 (PhC), 128.3, 128.0, 127.7 (PhCH), 91.5 (C-1), 69.1 ( $CH_2Ph$ ), 66.3, 59.6, 54.5, 53.5 (C-2, C-3, C-4, C-5), 25.8 ( $Me_3CSi$ ), -4.5, -4.6 ( $Me_2Si$ ).

Anal. Calcd for  $C_{18}H_{28}O_4Si$ : C, 64.24; H, 8.39. Found: C, 64.37; H, 8.28.

**Benzyl 2,3-Anhydro-4-O-formyl- $\beta$ -L-lyxopyranoside (10).** Benzyl 2,3-anhydro-4-O-[(trifluoromethyl)sulfonyl]- $\alpha$ -D-ribo-pyranoside (9, 708 mg, 2.00 mmol, prepared from 7 in 90% yield<sup>15</sup>) was converted into 10 as described in the preparation of 4. Column chromatography (E/H, 1:3) gave 10 (447 mg, 89%): mp 89.5–91.0 °C;  $[\alpha]_D^{20} +115^\circ$  (c 1.13,  $CHCl_3$ );  $^1H$  NMR  $\delta$  8.13 (m, 1 H, CHO), 7.37 (m, 5 H,  $C_6H_5$ ), 5.24 (m, 1 H, H-4), 5.10 (d, 1 H,  $J_{1,2} = 2.9$  Hz, H-1), 4.81, 4.63 (AB q, each 1 H,  $J_{A,B} = 12.2$  Hz,  $CH_2Ph$ ), 4.04, 3.58 (AB q with further couplings, each 1 H,  $J_{A,B} = 13.3$  Hz, H-5, H-5'), 3.39 (m, 2 H, H-2, H-3);  $^{13}C$  NMR  $\delta$  159.9 (CHO), 137.0 (PhC), 128.4, 128.2, 127.9 (PhCH), 91.6 (C-1), 69.4 ( $CH_2Ph$ ), 65.8, 58.6, 51.6, 48.9 (C-2, C-3, C-4, C-5); IR (KBr) 1730 (C=O), 1205, 1035  $cm^{-1}$ .

Anal. Calcd for  $C_{13}H_{14}O_5$ : C, 62.39; H, 5.64. Found: C, 62.25; H, 5.72.

**Benzyl 2,3-Anhydro- $\beta$ -L-lyxopyranoside (11).** Compound 9 (9.00 g, 25.4 mmol) was subjected to the same reaction conditions as described in the preparation of 5. Column chromatography (E/H, 1:2) gave 11 (4.84 g, 86%), which was recrystallized from ethyl acetate/hexane: mp 65.5–66.5 °C;  $[\alpha]_D^{20} +102^\circ$  (c 1.03,  $CHCl_3$ );  $^1H$  NMR  $\delta$  7.35 (m, 5 H,  $C_6H_5$ ), 5.04 (d, 1 H,  $J_{1,2} = 2.4$  Hz, H-1), 4.81, 4.62 (AB q, each 1 H,  $J_{A,B} = 12.4$  Hz,  $CH_2Ph$ ), 4.02 (m, 2 H, H-4, H-5), 3.46 (m, 1 H, H-5), 3.33 (m, 2 H, H-2, H-3), 2.09 (d, 1 H,  $J_{OH,4} = 9.5$  Hz, OH).

Anal. Calcd for  $C_{12}H_{14}O_4$ : C, 64.85; H, 6.35. Found: C, 64.90; H, 6.39.

**Benzyl 2,3-Anhydro-4-O-(tert-butylidimethylsilyl)- $\beta$ -L-lyxopyranoside (12).** Compound 11 (1.65 g, 7.43 mmol) was silylated as described in the preparation of 2. Column chromatography (E/H, 1:35) gave 12 (2.45 g, 98%): mp 46–47 °C;  $[\alpha]_D^{20} +71^\circ$  (c 0.88,  $CHCl_3$ );  $^1H$  NMR  $\delta$  7.35 (m, 5 H,  $C_6H_5$ ), 5.07 (d, 1 H,  $J_{1,2} = 2.8$  Hz, H-1), 4.82, 4.62 (AB q, each 1 H,  $J_{A,B} = 12.4$  Hz,  $CH_2Ph$ ), 4.03 (m, 1 H, H-4), 3.92, 3.35 (d AB q, each 1 H,  $J_{A,B} = 11.7$  Hz,  $J_{4,5}, J_{4,5'} = 2.8$  Hz, 2.8 Hz, H-5, H-5'), 3.33 (m, 1 H,  $J_{2,3} = 3.9$  Hz, H-2), 3.21 (dq, 1 H,  $J_{3,4} = 1.8$  Hz, H-3), 0.92 (s, 9 H,  $Me_3CSi$ ), 0.13 (2 s, each 3 H,  $Me_2Si$ );  $^{13}C$  NMR  $\delta$  137.4 (PhC), 128.3, 128.0, 127.7 (PhCH), 92.6 (C-1), 69.3 ( $CH_2Ph$ ), 64.4, 62.7, 52.6, 51.6 (C-2, C-3, C-4, C-5), 25.9 ( $Me_3CSi$ ), 18.3 ( $Me_3CSi$ ), -4.6 ( $Me_2Si$ ).

Anal. Calcd for  $C_{18}H_{28}O_4Si$ : C, 64.24; H, 8.39. Found: C, 64.26; H, 8.41.

**General Methods for the Oxirane Ring-Openings of 2, 6, 8 and 12.** All reactions were carried out in oven-dried flasks equipped with rubber septa and under an argon atmosphere. The organometallic reagents were transferred by dried, argon-flushed syringes. Solvents were predried with sodium wire and then stored over 4-Å molecular sieves for several days before use. The reaction mixtures were quenched by slow addition with vigorous stirring into cold aqueous ~2 M solutions of  $NH_4Cl$  (adjusted to pH ~8

(34) Magnusson, G.; Noori, G.; Dahmén, J.; Frejd, T. *Acta Chem. Scand., Ser. B* 1981, B35, 213.

(35) Ballou, C. E.; Roseman, S.; Link, K. P. *J. Am. Chem. Soc.* 1951, 73, 1140.

(36) Compound 7 was recrystallized several times from hexane/ethyl acetate without any change in the optical rotation. The  $^1H$  NMR spectrum corresponded with the data given in ref 14.

with 2 M  $\text{NH}_4\text{OH}$ ). 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 ( $\text{Na}_2\text{SO}_4$ ), and concentrated in vacuo (12 mmHg, water bath temperature  $\sim 35^\circ\text{C}$ ). The progress of the reactions was monitored by TLC analysis with ethyl acetate/heptane, 1:3, as eluent (all four 2-deoxy-2-C-methyl sugars gave relatively weak spots upon charring with 10%  $\text{H}_2\text{SO}_4$ ). The yields were determined by HPLC analysis of the crude products using calibration curves of the pure compounds in the concentration interval 7–21 mM. The HPLC solvent systems were ethyl acetate/hexane, 1:7 (A), 1:4 (B), 1:6 (C), and 1:9 (D).

**Benzyl  $\beta$ -L-glycero-Pent-3-enopyranoside (13), Benzyl 3-Deoxy-3-C-methyl-4-O-(tert-butyltrimethylsilyl)- $\beta$ -L-xylopyranoside (14), and Benzyl 2-Deoxy-2-C-methyl-4-O-(tert-butyltrimethylsilyl)- $\beta$ -L-arabinopyranoside (15).** (See Table II, entries 1–4.)

(a) Cuprous iodide (566 mg, 2.97 mmol) was suspended in diethyl ether (8 mL) and cooled to  $-40^\circ\text{C}$ . Ethereal MeLi (1.58 M, 3.76 mL, 5.94 mmol) was then added dropwise, and after 10 min, compound 2 (500 mg, 1.49 mmol), dissolved in diethyl ether (7 mL), was added to the homogeneous solution. The temperature was allowed to rise to  $0^\circ\text{C}$ , and after being stirred for 2 h, the solution was quenched and worked up as described under General Methods. HPLC (solvent A) analysis showed, 2 < 2%; 14, 30%; 15,  $\sim 0\%$ . It was not practical to determine by HPLC the yield of the major, polar product 13, which was isolated (oil, 208 mg, 68%) by column chromatography (E/H, 1:3). 13:  $R_f$  0.10;  $[\alpha]_D^{20} +274^\circ$  (c 1.10,  $\text{CHCl}_3$ );  $^1\text{H NMR } \delta$  7.36 (m, 5 H,  $\text{C}_6\text{H}_5$ ), 5.90 (AB q with further couplings, 2 H, H-3, H-4), 4.84, 4.61 (AB q, each 1 H,  $J_{A,B} = 12.0$  Hz,  $\text{CH}_2\text{Ph}$ ), 4.80 (d, 1 H,  $J_{1,2} = 2.7$  Hz, H-1), 4.26, 4.13 (AB q complex, each 1 H,  $J_{A,B} = 16.5$  Hz, H-5, H-5'), 3.93 (m, 1 H, H-2), 2.12 (d, 1 H,  $J_{2,\text{OH}} = 8.3$  Hz, OH);  $^{13}\text{C NMR } \delta$  137.2 (PhC), 128.8, 128.4, 127.9 (PhCH), 127.8, 124.4 (C-3, C-4), 99.7 (C-1), 70.0, 64.9, 60.8 (C-2, C-4,  $\text{CH}_2\text{Ph}$ ).

Anal. Calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_5$ : C, 69.88; H, 6.84. Found: C, 69.91; H, 6.88.

(b) Ethereal MeLi (1.60 M, 1.02 mL, 1.63 mmol) was added dropwise at room temperature to a solution of  $\text{Me}_3\text{Al}$  (817  $\mu\text{L}$ , 1.63 mmol) in hexane (3.0 mL). After 5 min, 2 (500 mg, 1.49 mmol) dissolved in hexane (10 mL) was added to the grayish suspension. The solution was refluxed for 24 h, cooled, and then worked up as described under General Methods. HPLC (solvent A) analysis showed 2,  $\sim 0\%$ ; 14, 82%; 15,  $\sim 0\%$ . Column chromatography (E/H, 1:6) yielded 14 (oil, 420 mg, 80%):  $R_f$  0.45;  $[\alpha]_D^{20} +72.9^\circ$  (c 1.10,  $\text{CHCl}_3$ );  $^1\text{H NMR } \delta$  7.33 (m, 5 H,  $\text{C}_6\text{H}_5$ ), 4.87, 4.56 (AB q, each 1 H,  $J_{A,B} = 11.4$  Hz,  $\text{CH}_2\text{Ph}$ ), 4.42 (d, 1 H,  $J_{1,2} = 6.0$  Hz, H-1), 3.92, 3.29 (d AB q, each 1 H,  $J_{A,B} = 11.2$  Hz,  $J_{4,5}, J_{4,5'} = 3.9$  Hz, 8.0 Hz, H-5, H-5'), 3.44 (m, 1 H,  $J_{3,4} = 8.1$  Hz, H-4), 3.21 (dq, 1 H,  $J_{2,3} = 8.5$  Hz,  $J_{2,\text{OH}} = 4.4$  Hz, H-2), 2.65 (d, 1 H, OH), 1.69 (m, 1 H, H-3), 1.13 (d, 3 H,  $J_{\text{Me}_3} = 7.0$  Hz, Me), 0.90 (s, 9 H,  $\text{Me}_3\text{CSi}$ ), 0.09, 0.07 (2 s, each 3 H,  $\text{Me}_2\text{Si}$ );  $^{13}\text{C NMR } \delta$  137.4 (PhC), 128.5, 128.0, 127.9 (PhCH), 103.0 (C-1), 73.0, 71.4, 70.6, 67.3 (C-2, C-4, C-5,  $\text{CH}_2\text{Ph}$ ), 42.2 (C-3), 25.8 ( $\text{Me}_3\text{CSi}$ ), 18.0 ( $\text{Me}_3\text{CSi}$ ), 14.4 (Me), -4.4, -4.8 ( $\text{Me}_2\text{Si}$ ).

Anal. Calcd for  $\text{C}_{19}\text{H}_{32}\text{O}_4\text{Si}$ : C, 64.73; H, 9.15. Found: C, 64.9; H, 9.3.

(c)  $\text{Me}_3\text{Al}$  (3.86 mL, 7.72 mmol) was rapidly added to a solution of 2 (2.00 g, 5.94 mmol) in hexane (50 mL) at room temperature. The solution was refluxed for 27 h, cooled, and then worked up as described under General Methods. HPLC (solvent A) analysis showed, 2 < 2%; 14, 11%; 15, 37%. Column chromatography (E/H, 1:25) gave 14 (oil, 212 mg, 10%) and 15 (oil, 727 mg, 35%). 15:  $R_f$  0.50;  $[\alpha]_D^{20} +161^\circ$  (c 1.38,  $\text{CHCl}_3$ );  $^1\text{H NMR } \delta$  7.33 (m, 5 H,  $\text{C}_6\text{H}_5$ ), 4.76 (d, 1 H,  $J_{1,2} = 3.4$  Hz, H-1), 4.71, 4.45 (AB q, each 1 H,  $J_{A,B} = 12.2$  Hz,  $\text{CH}_2\text{Ph}$ ), 3.89–3.60 (m, 4 H, H-3, H-4, H-5, H-5'), 2.04 (m, 1 H, H-2), 1.87 (d, 1 H,  $J_{3,\text{OH}} = 10.3$  Hz, OH), 1.05 (d, 3 H,  $J_{\text{Me}_2} = 7.2$  Hz, Me), 0.93 (s, 9 H,  $\text{Me}_3\text{CSi}$ ), 0.13, 0.12 (2 s, each 3 H,  $\text{Me}_2\text{Si}$ );  $^{13}\text{C NMR } \delta$  138.1 (PhC), 128.3, 127.5 (PhCH), 100.3 (C-1), 70.4, 69.3, 69.1, 63.8 (C-3, C-4, C-5,  $\text{CH}_2\text{Ph}$ ), 37.4 (C-2), 25.8 ( $\text{Me}_3\text{CSi}$ ), 18.1 ( $\text{Me}_3\text{CSi}$ ), 12.2 (Me), -4.4, -4.8 ( $\text{Me}_2\text{Si}$ ).

Anal. Calcd for  $\text{C}_{19}\text{H}_{32}\text{O}_4\text{Si}$ : C, 64.73; H, 9.15. Found: C, 64.88; H, 9.14.

In order to obtain additional proof of the structure of 15 by NMR, we acetylated it (pyridine/acetic anhydride, 3:2,  $20^\circ\text{C}$ , 24 h), and the resulting acetate was purified by column chro-

matography (E/H, 1:10) to give the 3-O-acetate of 15 (oil, 92%):  $^1\text{H NMR } \delta$  4.95 (dd, 1 H,  $J_{2,3} = 11.2$  Hz,  $J_{3,4} = 2.9$  Hz, H-3), 4.78 (d, 1 H,  $J_{1,2} = 3.3$  Hz, H-1), 4.01 (m, 1 H, H-4), 3.90, 3.54 (d AB q, each 1 H,  $J_{A,B} = 12.0$  Hz,  $J_{4,5}, J_{4,5'} = 0.8$  Hz, 2.6 Hz, H-5, H-5'), 2.45 (m, 1 H, H-2), 0.93 (d, 3 H,  $J_{\text{Me}_2} = 7.1$  Hz, Me).

(d) Ethereal  $\text{Me}_2\text{Mg}$  (9.28 mL, 5.94 mmol) was added to a solution of 2 (100 mg, 297  $\mu\text{mol}$ ) in diethyl ether (1.0 mL). The solution was refluxed for 48 h, cooled, and then worked up as described under General Methods. HPLC (solvent A) analysis showed 2,  $\sim 0\%$ ; 14, 12%; 15, 9%.

**Benzyl 3-Deoxy-3-C-methyl-4-O-(tert-butyltrimethylsilyl)- $\alpha$ -D-arabinopyranoside (16) and Benzyl 2-Deoxy-2-C-methyl-4-O-(tert-butyltrimethylsilyl)- $\alpha$ -D-xylopyranoside (17).** (See Table II, entries 5–9.)

(a) Cuprous iodide (707 mg, 3.71 mmol) was suspended in 2.5 mL of diethyl ether and cooled to  $0^\circ\text{C}$ . Ethereal MeLi (1.64 M, 4.53 mL, 7.43 mmol) was added dropwise, to give a homogeneous solution. After 5 min, 6 (250 mg, 743  $\mu\text{mol}$ ), dissolved in diethyl ether (4.0 mL), was added. The ice bath was removed after 1 h, and the solution was stirred for 28 h at room temperature and then worked up as described under General Methods. HPLC (solvent B) analysis showed 6, 9%; 16,  $\sim 0\%$ ; 17, 70%. Column chromatography (E/H, 1:10) gave 17 (182 mg, 69%), which was recrystallized from ethanol/water:  $R_f$  0.49; mp 62–63  $^\circ\text{C}$ ;  $[\alpha]_D^{20} +111^\circ$  (c 0.96,  $\text{CHCl}_3$ );  $^1\text{H NMR } \delta$  7.35 (m, 5 H,  $\text{C}_6\text{H}_5$ ), 4.72, 4.43 (AB q, each 1 H,  $J_{A,B} = 12.2$  Hz,  $\text{CH}_2\text{Ph}$ ), 4.68 (d, 1 H,  $J_{1,2} = 3.5$  Hz, H-1), 3.60–3.54 (m, 4 H, H-3, H-4, H-5, H-5'), 2.18 (br s, 1 H, OH), 1.79 (m, 1 H, H-2), 1.08 (d, 3 H,  $J_{\text{Me}_2} = 6.8$  Hz, Me), 0.90 (s, 9 H,  $\text{Me}_3\text{CSi}$ ), 0.12, 0.09 (2 s, each 3 H,  $\text{Me}_2\text{Si}$ );  $^{13}\text{C NMR } \delta$  137.9 (PhC), 128.3, 127.6 (PhCH), 100.0 (C-1), 74.6, 73.2, 68.8, 62.6 (C-3, C-4, C-5,  $\text{CH}_2\text{Ph}$ ), 40.4 (C-2), 25.7 ( $\text{Me}_3\text{CSi}$ ), 18.0 ( $\text{Me}_3\text{CSi}$ ), 12.4 (Me), -4.4, -4.7 ( $\text{Me}_2\text{Si}$ ).

Anal. Calcd for  $\text{C}_{19}\text{H}_{32}\text{O}_4\text{Si}$ : C, 64.73; H, 9.15. Found: C, 64.79; H, 9.14.

In order to obtain additional proof of the structure of 17 by NMR, we acetylated it (pyridine/acetic anhydride, 3:2,  $20^\circ\text{C}$ , 24 h), and the resulting acetate was purified by column chromatography (E/H, 1:10) to give the 3-O-acetate of 17 (oil, 95%):  $^1\text{H NMR } \delta$  5.11 (dd, 1 H,  $J_{2,3} = 11.2$  Hz,  $J_{3,4} = 8.1$  Hz, H-3), 4.68 (d, 1 H,  $J_{1,2} = 3.4$  Hz, H-1), 3.74–3.56 (m, 3 H, H-4, H-5, H-5'), 1.85 (m, 1 H, H-2), 0.92 (d, 3 H,  $J_{\text{Me}_2} = 6.8$  Hz, Me).

(b) Ethereal MeLi (1.60 M, 1.02 mL, 1.63 mmol) was added dropwise to  $\text{Me}_3\text{Al}$  (408  $\mu\text{L}$ , 816  $\mu\text{mol}$ ) at  $0^\circ\text{C}$ . After 5 min, 6 (250 mg, 743  $\mu\text{mol}$ ) dissolved in hexane (5.0 mL) was added. The ice bath was removed after 20 min, and the solution was stirred at room temperature for another 3 h. Quenching and work up were then performed as described under General Methods. HPLC (solvent B) analysis showed 6, 6%; 16,  $\sim 0\%$ ; 17, 84%. Column chromatography (E/H, 1:10) yielded 17 (221 mg, 84%).

(c)  $\text{Me}_3\text{Al}$  (483  $\mu\text{L}$ , 966  $\mu\text{mol}$ ) was added to a solution of 6 (250 mg, 743  $\mu\text{mol}$ ) in hexane (7.0 mL) at room temperature. The solution was refluxed for 24 h, cooled, and then worked up as described under General Methods. HPLC (solvent B) analysis showed 6,  $\sim 0\%$ ; 16, 56%; 17,  $\sim 2\%$ . Column chromatography (E/H, 1:8) gave 16 (oil, 141 mg, 54%):  $R_f$  0.35;  $[\alpha]_D^{20} +0.6^\circ$  (c 0.95,  $\text{CHCl}_3$ );  $^1\text{H NMR } \delta$  7.36 (m, 5 H,  $\text{C}_6\text{H}_5$ ), 4.93, 4.58 (AB q, each 1 H,  $J_{A,B} = 11.7$  Hz,  $\text{CH}_2\text{Ph}$ ), 4.24 (d, 1 H,  $J_{1,2} = 7.0$  Hz, H-1), 3.86, 3.53 (d AB q, each 1 H,  $J_{A,B} = 12.2$  Hz,  $J_{4,5}, J_{4,5'} = 1.4$  Hz, 2.3 Hz, H-5, H-5'), 3.69 (m, 1 H, H-4), 3.53 (m, 1 H,  $J_{2,3} = 10.3$  Hz,  $J_{2,\text{OH}} = 2.4$  Hz, H-2), 2.09 (d, 1 H, OH), 1.67 (m, 1 H,  $J_{3,4} = 3.2$  Hz, H-3), 1.09 (d, 3 H,  $J_{\text{Me}_3} = 6.5$  Hz, Me), 0.92 (s, 9 H,  $\text{Me}_3\text{CSi}$ ), 0.08, 0.06 (2 s, each 3 H,  $\text{Me}_2\text{Si}$ );  $^{13}\text{C NMR } \delta$  137.6 (PhC), 128.5, 128.0, 127.9 (PhCH), 104.0 (C-1), 71.4, 70.5, 70.3, 69.9 (C-2, C-4, C-5,  $\text{CH}_2\text{Ph}$ ), 40.5 (C-3), 25.9 ( $\text{Me}_3\text{CSi}$ ), 18.2 ( $\text{Me}_3\text{CSi}$ ), 13.6 (Me), -4.3, -4.9 ( $\text{Me}_2\text{Si}$ ).

Anal. Calcd for  $\text{C}_{19}\text{H}_{32}\text{O}_4\text{Si}$ : C, 64.73; H, 9.15. Found: C, 64.75; H, 9.20.

(d) Compound 6 (100 mg, 297  $\mu\text{mol}$ ) was treated with  $\text{Me}_2\text{Mg}$  as described in the reaction of 2, experiment d, except that the reaction mixture was refluxed for 69 h. HPLC (solvent B) analysis showed 6,  $\sim 0\%$ ; 16, 80%; 17, 8%. Column chromatography (E/H, 1:10) yielded 16 (84 mg, 80%).

**Benzyl 2-Deoxy-2-C-methyl-4-O-(tert-butyltrimethylsilyl)- $\alpha$ -D-arabinopyranoside (18) and Benzyl 3-Deoxy-3-C-methyl-4-O-(tert-butyltrimethylsilyl)- $\alpha$ -D-xylopyranoside (19).** (See Table II, entries 10–14.)



(a) Compound **8** (500 mg, 1.49 mmol) was treated with  $\text{Me}_2\text{CuLi}$  (1.1 equiv) as described in the reaction of **2**, experiment a, except that the reaction mixture was kept at 0 °C for 35 min. HPLC (solvent C) analysis showed **8**, ~0%; **18**, 38%; **19**, 43%.

(b) Compound **8** (500 mg, 1.49 mmol) was treated with  $\text{Me}_4\text{AlLi}$  (1.1 equiv) as described in the reaction of **2**, experiment b, except that the reaction mixture was refluxed for 5 h. HPLC (solvent C) analysis showed **8**, ~0%; **18**, 48%; **19**, 48%.

(c) Ethereal  $\text{MeLi}$  (1.64 M, 38.3 mL, 62.8 mmol) was slowly added to  $\text{Me}_3\text{Al}$  (15.7 mL, 31.4 mmol) at room temperature. After 10 min, hexane (100 mL) and then **8** (9.60 g, 28.5 mmol), dissolved in hexane (100 mL), were added. The solution was refluxed for 50 min, cooled, diluted with diethyl ether (50 mL), injected into a rapidly stirred cold (0 °C) aqueous solution of  $\text{NH}_4\text{Cl}$  (~2 M, 450 mL, adjusted to ~pH 8 with 2 M  $\text{NH}_4\text{OH}$ ), and then worked up as described under General Methods. HPLC (solvent C) analysis showed **8**, ~0%; **18**, 67%; **19**, 15%. Column chromatography (E/H, 1:15) yielded **18** (semicrystalline, 6.62 g, 66%) and **19** (oil, 1.36 g, 14%). **18**:  $R_f$  0.48;  $[\alpha]_D^{20} +56.1^\circ$  (c 1.00,  $\text{CHCl}_3$ );  $^1\text{H NMR}$   $\delta$  7.34 (m, 5 H,  $\text{C}_6\text{H}_5$ ), 4.83, 4.53 (AB q, each 1 H,  $J_{A,B} = 12.3$  Hz,  $\text{CH}_2\text{Ph}$ ), 4.24 (d, 1 H,  $J_{1,2} = 4.4$  Hz, H-1), 3.93, 3.45 (d AB q, each 1 H,  $J_{A,B} = 11.9$  Hz,  $J_{4,5}, J_{4,5'} = 2.9$  Hz, 5.8 Hz, H-5, H-5'), 3.85 (m, 1 H, H-4), 3.39 (m, 1 H,  $J_{3,4} = 3.4$  Hz,  $J_{2,3} = 7.3$  Hz,  $J_{3,\text{OH}} = 9.3$  Hz, H-3), 2.44 (d, 1 H, OH), 2.04 (m, 1 H, H-2), 1.05 (d, 3 H,  $J_{\text{Me},2} = 7.1$  Hz, Me), 0.93 (s, 9 H,  $\text{Me}_3\text{CSi}$ ), 0.13, 0.12 (2 s, each 3 H,  $\text{Me}_2\text{Si}$ );  $^{13}\text{C NMR}$   $\delta$  137.6 (PhC), 128.4, 127.9, 127.7 (PhCH), 102.1 (C-1), 73.2, 69.7, 67.3, 63.6 (C-3, C-4, C-5,  $\text{CH}_2\text{Ph}$ ), 39.3 (C-2), 25.8 ( $\text{Me}_3\text{CSi}$ ), 18.2 ( $\text{Me}_3\text{CSi}$ ), 13.5 (Me), -4.4, -4.8 ( $\text{Me}_2\text{Si}$ ).

Anal. Calcd for  $\text{C}_{19}\text{H}_{32}\text{O}_4\text{Si}$ : C, 64.73; H, 9.15. Found: C, 64.80; H, 9.19.

**19**:  $R_f$  0.41;  $[\alpha]_D^{20} +84.1^\circ$  (c 1.40,  $\text{CHCl}_3$ );  $^1\text{H NMR}$   $\delta$  7.35 (m, 5 H,  $\text{C}_6\text{H}_5$ ), 4.81 (d, 1 H,  $J_{1,2} = 3.9$  Hz, H-1), 4.80, 4.51 (AB q, each 1 H,  $J_{A,B} = 11.8$  Hz,  $\text{CH}_2\text{Ph}$ ), 3.52–3.49 (m, 2 H, H-5, H-5'), 3.34 (m, 1 H, H-4), 3.22 (dt, 1 H,  $J_{2,3} = 10.8$  Hz,  $J_{2,\text{OH}} = 11.5$  Hz, H-2), 1.76 (m, 1 H, H-3), 1.10 (d, 3 H,  $J_{\text{Me},3} = 6.3$  Hz, Me), 0.89 (s, 9 H,  $\text{Me}_3\text{CSi}$ ), 0.08, 0.06 (2 s, each 3 H,  $\text{Me}_2\text{Si}$ );  $^{13}\text{C NMR}$   $\delta$  137.4 (PhC), 128.5, 128.0, 127.9 (PhCH), 96.7 (C-1), 72.6, 71.2, 69.3, 63.6 (C-2, C-4, C-5,  $\text{CH}_2\text{Ph}$ ), 41.5 (C-2), 25.7 ( $\text{Me}_3\text{CSi}$ ), 18.0 ( $\text{Me}_3\text{CSi}$ ), 13.9 (Me), -4.3, -4.8 ( $\text{Me}_2\text{Si}$ ).

Anal. Calcd for  $\text{C}_{19}\text{H}_{32}\text{O}_4\text{Si}$ : C, 64.73; H, 9.15. Found: C, 64.6; H, 9.2.

In order to obtain additional proof of the structure of **19** by NMR, we acetylated it (pyridine/acetic anhydride, 3:2, 20 °C, 24 h), and the resulting acetate was purified by column chromatography (E/H, 1:14) to give the 2-*O*-acetate of **19** (oil, 96%):  $^1\text{H NMR}$   $\delta$  4.87 (d, 1 H,  $J_{1,2} = 3.4$  Hz, H-1), 4.52 (dd, 1 H,  $J_{2,3} = 11.6$  Hz, H-2), 3.55, 3.53 (AB q, each 1 H,  $J_{4,5}, J_{4,5'} = 5.1$  Hz, 10.5 Hz, H-5, H-5'), 3.41 (m, 1 H,  $J_{3,4} = 9.4$  Hz, H-4), 2.12 (m, 1 H, H-2), 0.98 (d, 3 H,  $J_{\text{Me},3} = 6.7$  Hz, Me).

(d) Compound **8** (500 mg, 1.49 mmol) was treated with  $\text{Me}_3\text{Al}$  (4.0 equiv) as described in the reaction of **2**, experiment c, except that the reaction mixture was refluxed for 45 h. HPLC (solvent C) analysis showed **8**, ~0%; **18**, ~0%; **19**, 38%. Column chromatography (E/H, 1:10) yielded **19** (199 mg, 38%).

(e) Compound **8** (300 mg, 892  $\mu\text{mol}$ ) was dissolved in diethyl ether (30 mL), and then ethereal  $\text{Me}_2\text{Mg}$  (2.79 mL, 1.78 mmol) was added at room temperature. The solution was refluxed for 45 h, cooled, and then worked up as described under General Methods. HPLC (solvent C) analysis showed **8**, 14%; **18**, ~3%; **19**, 13%.

**Benzyl 2-Deoxy-2-*C*-methyl-4-*O*-(*tert*-butyldimethylsilyl)- $\beta$ -L-xylopyranoside (**20**) and Benzyl 3-Deoxy-3-*C*-methyl-4-*O*-(*tert*-butyldimethylsilyl)- $\beta$ -L-arabinopyranoside (**21**).** (See Table II, entries 15–18.)

(a) Compound **12** (250 mg, 743  $\mu\text{mol}$ ) was treated with  $\text{Me}_2\text{CuLi}$  (3.0 equiv) as described for the reaction of **6**, experiment a, except that the reaction mixture was kept at 0 °C for 3 h before quenching. HPLC (solvent D) analysis showed **12**, <2%; **20**, 76%; **21**, ~2%. Since it was difficult to purify **20** chromatographically, the crude product was acetylated (2 h, 22 °C) in pyridine/acetic anhydride, 3:2 (5.0 mL) and then the acetate was column chromatographed (E/H, 1:30) to yield the 3-*O*-acetate of **20** (oil, 214 mg, 73% from **12**). The 3-*O*-acetate (50 mg, 127  $\mu\text{mol}$ ) was then deacetylated with hydrazine hydrate (99.5%)/ethanol, 1:1 (50 °C, 20 h). After concentration in vacuo, the residue was chromatographed (E/H, 1:10) to yield **20** (syrup, 31 mg, 68%):  $R_f$  0.51;  $[\alpha]_D^{20} +81.8^\circ$  (c 0.91,  $\text{CHCl}_3$ );  $^1\text{H NMR}$   $\delta$  7.35 (m, 5 H,  $\text{C}_6\text{H}_5$ ), 4.86, 4.56 (AB q, each 1 H,  $J_{A,B} = 11.9$  Hz,  $\text{CH}_2\text{Ph}$ ), 4.20 (d, 1 H,  $J_{1,2} = 7.7$  Hz, H-1), 3.92, 3.19 (d AB q, each 1 H,  $J_{A,B} = 11.5$  Hz,  $J_{4,5}, J_{4,5'} = 4.8$  Hz, 9.2 Hz, H-5, H-5'), 3.58 (m, 1 H,  $J_{3,4} = 7.8$  Hz, H-4), 3.18 (dd, 1 H,  $J_{2,3} = 9.6$  Hz, H-3), 2.4 (br s, 1 H, OH), 1.74 (m, 1 H, H-2), 1.09 (d, 3 H,  $J_{\text{Me},2} = 6.6$  Hz, Me), 0.89 (s, 9 H,  $\text{Me}_3\text{CSi}$ ), 0.10, 0.09 (2 s, each 3 H,  $\text{Me}_2\text{Si}$ );  $^{13}\text{C NMR}$   $\delta$  137.5 (PhC), 128.4, 128.0, 127.8 (PhCH), 103.6 (C-1), 76.9, 72.2, 70.5, 65.6 (C-3, C-4, C-5,  $\text{CH}_2\text{Ph}$ ), 41.4 (C-2), 25.7 ( $\text{Me}_3\text{CSi}$ ), 18.0 ( $\text{Me}_3\text{CSi}$ ), 12.8 (Me), -4.5, -4.7 ( $\text{Me}_2\text{Si}$ ).

Anal. Calcd for  $\text{C}_{19}\text{H}_{32}\text{O}_4\text{Si}$ : C, 64.73; H, 9.15. Found: C, 64.76; H, 9.12.

(b) Compound **12** (250 mg, 743  $\mu\text{mol}$ ) was treated with  $\text{Me}_4\text{AlLi}$  as described for the reaction of **2**, experiment b, except that the reaction mixture was refluxed for 4 h before quenching. HPLC (solvent D) analysis showed **12**, <2%; **20**, 88%; **21**, ~0%. The crude product was acetylated and chromatographed as described for **12**, experiment a, to yield the 3-*O*-acetate of **20** (235 mg, 80%). Deacetylation yielded **20** (68%).

(c) Compound **12** (100 mg, 297  $\mu\text{mol}$ ) was treated with  $\text{Me}_3\text{Al}$  (2.6 equiv) as described in the reaction of **2**, experiment c, except that the reaction mixture was refluxed for 48 h before quenching. HPLC (solvent D) analysis showed **12**, ~0%; **20**, 3%; **21**, 49%. Column chromatography (E/H, 1:16) gave **21** (oil, 49 mg, 47%):  $R_f$  0.47;  $[\alpha]_D^{20} +162^\circ$  (c 1.02,  $\text{CHCl}_3$ );  $^1\text{H NMR}$   $\delta$  7.35 (m, 5 H,  $\text{C}_6\text{H}_5$ ), 4.92 (d, 1 H,  $J_{1,2} = 3.7$  Hz, H-1), 4.78, 4.52 (AB q, each 1 H,  $J_{A,B} = 11.7$  Hz,  $\text{CH}_2\text{Ph}$ ), 3.79, 3.49 (d AB q, each 1 H,  $J_{A,B} = 11.7$  Hz,  $J_{4,5}, J_{4,5'} = 1.2$  Hz, 2.0 Hz, H-5, H-5'), 3.71 (m, 1 H, H-4), 3.67 (dt, 1 H,  $J_{2,3} = 11.2$  Hz,  $J_{2,\text{OH}} = 11.1$  Hz, H-2), 1.91 (m, 1 H,  $J_{3,4} = 2.6$  Hz, H-3), 1.65 (d, 1 H, OH), 1.06 (d, 3 H,  $J_{\text{Me},3} = 6.7$  Hz, Me), 0.92 (s, 9 H,  $\text{Me}_3\text{CSi}$ ), 0.07, 0.06 (2 s, each 3 H,  $\text{Me}_2\text{Si}$ );  $^{13}\text{C NMR}$   $\delta$  137.7 (PhC), 128.5, 127.9, 127.8 (PhCH), 97.7 (C-1), 71.0, 69.6, 69.4, 65.0 (C-2, C-4, C-5,  $\text{CH}_2\text{Ph}$ ), 37.1 (C-3), 25.8 ( $\text{Me}_3\text{CSi}$ ), 18.1 ( $\text{Me}_3\text{CSi}$ ), 13.9 (Me), -4.5, -4.9 ( $\text{Me}_2\text{Si}$ ).

Anal. Calcd for  $\text{C}_{19}\text{H}_{32}\text{O}_4\text{Si}$ : C, 64.73; H, 9.15. Found: C, 64.80; H, 9.20.

(d) Compound **12** (100 mg, 297  $\mu\text{mol}$ ) was treated with  $\text{Me}_2\text{Mg}$  (20 equiv) as described in the reaction of **2**, experiment d, except that the reaction mixture was refluxed for 66 h before quenching. HPLC (solvent D) analysis showed **12**, <5%; **20**, 52%; **21**, 28%.

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