Regioselective Ring Opening of Selected Benzylidene Acetals. A Photochemically Inititated Reaction for Partial Deprotection of Carbohydrates

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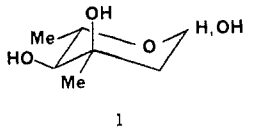
A new method is described for regioselective partial deprotection of carbohydrates protected as benzylidene acetals. This deprotection was accomplished for each of the six methyl pyranosides (**4**, **5**, and **18**–**21**) studied by irradiation of the protected sugar and *N*-bromosuccinimide (NBS) in the presence of water. Under these conditions the benzylidene (1,3-dioxolane) ring in each compound opened to give a methyl pyranoside with an axial benzoyloxy group and an equatorial hydroxy group. For example, irradiation of methyl 3,4-*O*-benzylidene (*R* or *S*)-6-deoxy-2-*O*-(2,2-dimethylpropanoyl)-α-L-galactopyranoside (**18** or **19**) with NBS, barium carbonate, and water resulted in the formation of methyl 4-*O*-benzoyl-6-deoxy-2-*O*-(2,2-dimethylpropanoyl)-α-L-galactopyranoside (**22**) in 72% yield. In a similar manner compounds **4** and **5** gave **10** and compounds **20** and **21** produced **23**. The advantages of this deprotection process are described.

Introduction

Among the essential components of many macrolide antibiotics is a group of compounds which are classified as branched-chain, deoxy sugars.[1] Frequently, these sugars are 2,6-dideoxy-L-hexoses which have a methyl branch at C-3.[2] L-Mycarose (**1**) is a typical example of one of these compounds.



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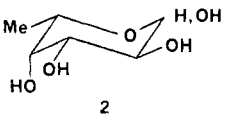

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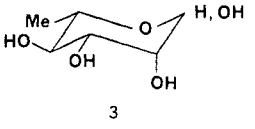

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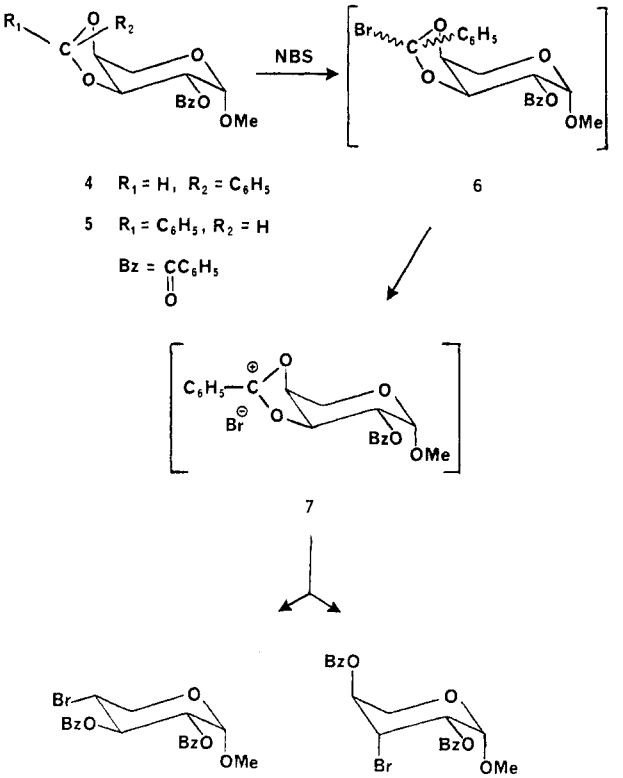
Laboratory syntheses of L-mycarose (**1**)[3] and other methyl-branched, 2,6-dideoxy-L-hexoses[4] have been accomplished by several research groups. Quite different starting materials and procedures have been used. When one considers the possibility of a general approach to the synthesis of these compounds, it is clear that the two most readily available L-hexoses, 6-deoxy-L-galactose (L-fucose, **2**) and 6-deoxy-L-mannose (L-rhamnose, **3**), both are reasonable starting materials for the synthesis of all branched-chain 2,6-dideoxy-L-hexoses. With either of these starting materials (**2** or **3**), however, an obstacle to be overcome prior to branch-chain introduction is a selective protection which leaves only the C-3 hydroxyl unprotected. In this paper we describe a simple procedure for accomplishing this necessary selective protection. While attention is focused here on three specific applications of this procedure, the process itself appears to be one which could be useful in a variety of instances where selective protection is required.

Scheme I



Seventeen years ago Hanessian,[5] and Hullar and Siskin,[6] independently reported a promising new reaction for the formation of bromodeoxy sugars. This reaction, which takes place when an *O*-benzylidene-protected sugar is treated with *N*-bromosuccinimide (NBS) in refluxing carbon tetrachloride, subsequently was studied extensively by Hanessian and Pleassas[7] and now has become a valuable standard tool in carbohydrate synthesis. An example of the reaction is given in Scheme I.

(1) Grisebach, H. *Adv. Carbohydr. Chem. Biochem.* **1978**, *35*, 81.
(2) Grisebach, H.; Schmid, R. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 159.
(3) (a) Lemal, D. M.; Pacht, P. D.; Woodward, R. B. *Tetrahedron* **1962**, *18*, 1275. (b) Howarth, G. B.; Jones, J. K. N. *Can. J. Chem.* **1967**, *45*, 2253. (c) Thiem, J.; Elvers, J. *Chem. Ber.* **1978**, *111*, 3514. (d) Fuganti, C.; Grasselli, P. *J. Chem. Soc., Chem. Commun.* **1978**, 299.
(4) (a) Williams, E. H.; Szarek, W. A.; Jones, J. K. N. *Can. J. Chem.* **1969**, *47*, 4467. (b) Garegg, P. J.; Norberg, T. *Acta Chem. Scand. Ser. B* **1975**, *29*, 507. (c) Fuganti, C.; Grasselli, P.; Marinoni, G. *Tetrahedron Lett.* **1979**, 1161.
(5) Hanessian, S. *Carbohydr. Res.* **1966**, *2*, 86.
(6) (a) Failla, D. L.; Hullar, T. L.; Siskin, S. B. *J. Chem. Soc., Chem. Commun.* **1966**, 716. (b) Hullar, T. L.; Siskin, S. B. *J. Org. Chem.* **1970**, *35*, 225.
(7) Hanessian, S.; Pleassas, N. R. *J. Org. Chem.* **1969**, *34*, 1035, 1045, and 1053.

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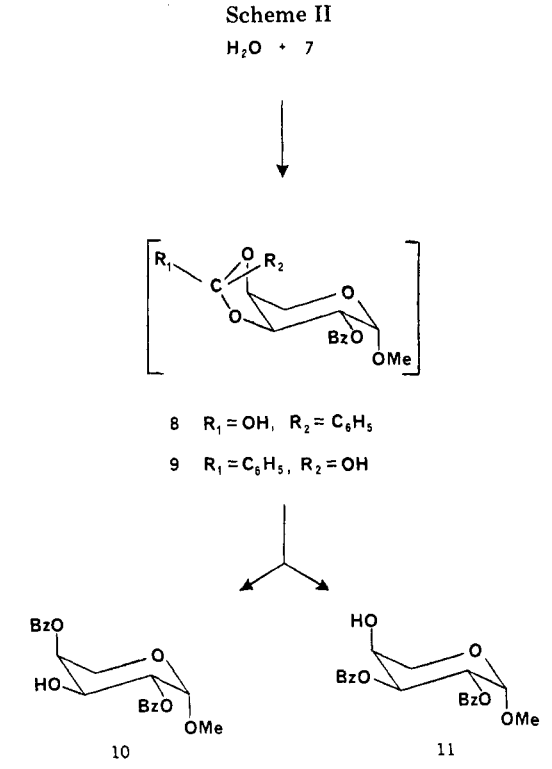
Scheme II



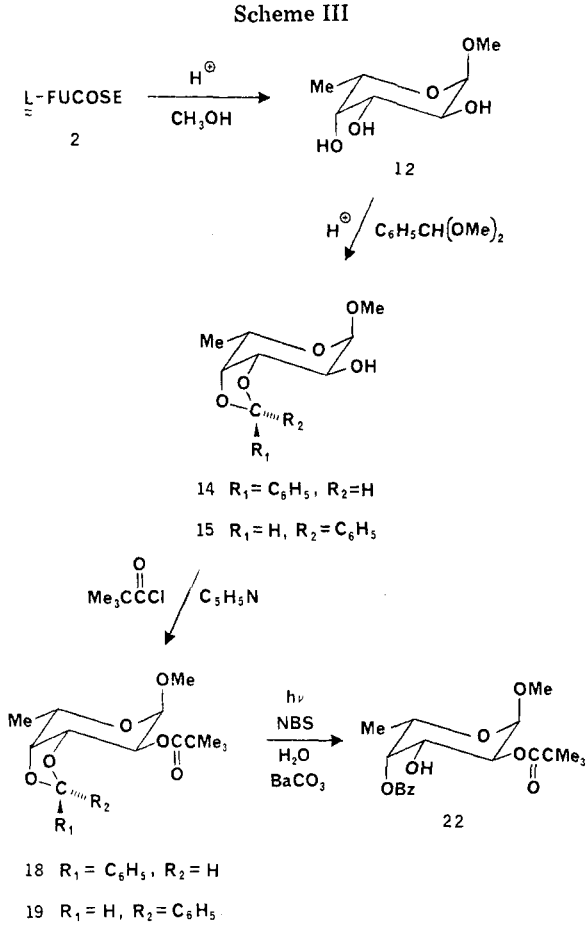
Carbocation intermediates have been proposed for this process; for example, the reaction of **4** or **5** with NBS is thought to produce the unstable bromo derivatives **6** and then the carbocation **7** (Scheme I).[8a] If **7** is an intermediate in this process, it should be possible to intercept it by reaction with water *prior to ring opening*. (Hanessian and Pleassas, in fact, showed that addition of water to a typical reaction mixture reduced the bromodeoxy sugar yield.)[8b] Reaction with water should produce one or both of the unstable compounds **8** and **9** (Scheme II). These compounds (**8** and **9**) then should experience opening of the 1,3-dioxalane ring. Ring opening of compounds similar to **8** and **9** is known to be highly regioselective.[9] The factors responsible for this regioselectivity have been analyzed.[9,10] The conclusions reached can be translated into the following simple predictive principle: when the hydroxyl group attached to the benzylic carbon in a compound such as **8** is exo to the pyranose ring, the dioxalane ring will open to give an axial benzoate (i.e., compound **10**). If the hydroxyl group is endo (**9**), the equatorial benzoate (**11**) will be produced.

It is generally the case that attack on a carbocation such as **7** by a water molecule will occur on the least hindered side of the cation; therefore, water should react with **7** to give **8**. (Compound **8** then would be expected to ring open to give the 2,4-dibenzoate **10**). The carbocation **7** has, in fact, been generated independently and shown to react with water to give **10**.[11]

Results and Discussion

With this information about dioxalane ring opening in mind, we decided to investigate the reaction of the benzylidene acetals **4** and **5** with NBS in the presence of water.

Scheme III



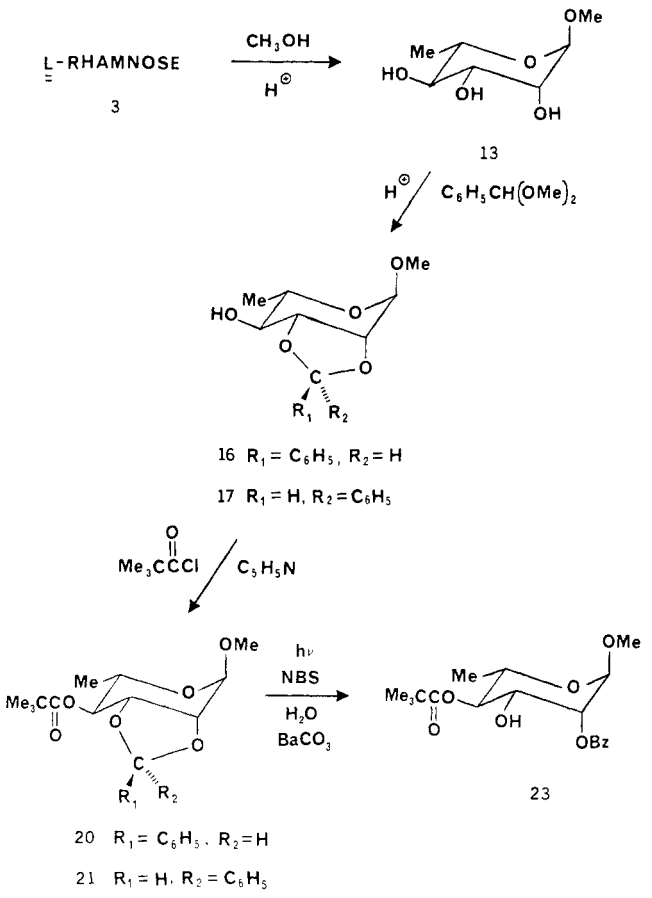
Compounds **4** and **5** were selected for this initial study not only because they are easily synthesized but also because the possible dibenzoate products **10** and **11** are well characterized. Each starting material (**4** and **5**) was dissolved separately in carbon tetrachloride to which NBS, barium carbonate, and water had been added and each reaction mixture was irradiated with a low-pressure, mercury lamp for 2.5 h. Product isolation in both cases afforded only the 2,4-dibenzoate **10** (62% yield), that is, only the product expected from reaction of the carbocation **7** with water. (No 2,3-dibenzoate (**11**) was detected.) The regiospecific formation of **10** from **4** and **5** suggested that similar reactions would be observed with comparable derivatives of L-fucose (**2**) and L-rhamnose (**3**).

The *O*-benzylidene protected L-fucose derivatives **14** and **15** and L-rhamnose derivatives **16** and **17** were synthesized as outlined in Schemes III and IV. Formation of the methyl glycosides **12** and **13** was maximized in each case (>90% yield) by the following procedure: glycoside formation, selective crystallization from the anomeric mixtures, reequilibration of the noncrystalline material, and repeated selective crystallization. The *O*-benzylidene sugars **14**–**17** were prepared by treatment of **12** and **13** with α,α-dimethoxytoluene.[12] This procedure produced diastereomeric mixtures (**14** with **15** and **16** with **17**) which were separated into their individual components for identification purposes; however, for light-initiated ring opening of these compounds with NBS and water, separation was unnecessary since **14** and **15** were to be converted into the same compound (**22**) and the diasteromers **16** and **17** both were to be transformed into compound **23**.

Prior to benzylidene ring opening, compounds **14**–**17** were esterified with pivaloyl chloride. This esterification

(8) (a) Reference 7, p 1055. (b) Reference 7, p 1039.
(9) King, J. F.; Allbutt, A. D. *Can. J. Chem.* **1969**, *47*, 1445; *Ibid.* **1970**, *48*, 1754.
(10) (a) Deslongchamps, P.; Atlani, P.; Frehel, D.; Malaval, A. *Can. J. Chem.* **1972**, *50*, 3405. (b) Deslongchamps, P.; Moreau, C.; Frehel, D.; Chenevert, R. *Ibid.* **1975**, *53*, 1204.
(11) Jacobsen, S.; Pedersen, C. *Acta. Chem. Scand. Ser. B* **1974**, *28*, 866.
(12) Evans, M. E. *Methods Carbohydr. Chem.* **1980**, *8*, 313.

Scheme IV



was conducted so that after ring opening, the oxygens at C-2 and C-4 in compounds **22** and **23** would be part of ester groups with quite different reactivities. For further transformations of compounds **22** and **23** selective ester group removal would be advantageous.

Reaction of the L-fucose derivatives **18** and **19**, either separately or as a mixture, with NBS, barium carbonate, and water in the presence of UV radiation, gave a single, carbohydrate-containing compound in 72% yield. The previously observed direction of ring opening for the arabinose derivatives **4** and **5** made compound **22** the probable choice for the ring-open product from **18** and **19**. The assignment of structure in this case was made by a combination of chemical and spectroscopic evidence. First, base-catalyzed reaction of this product with methanol regenerated methyl α-L-fucopyranoside (**12**); thus, the basic structure of the molecule was unchanged by the protection and deprotection reactions. The ^{13}C and ^{1}H NMR spectra (Tables I and II) confirmed the presence of a pivaloyl group and a benzoyl group in the molecule. The location of the benzoyl group was determined by analysis of the ^{1}H NMR spectrum. The ring-opening process could place the benzoyloxy substituent either on C-3 or C-4. A decision concerning the location of this group was made by considering the chemical shifts of H-3 and H-4 after dioxalane ring opening. A proton bound to a benzoyloxy-substituted carbon resonates further downfield than a similar proton attached to a hydroxy-substituted carbon.[13] The chemical shift for H-4 in the product was at δ 5.38 while that for H-3 was at 4.25; thus, the benzoyloxy group was attached to C-4 and the ring-opening reaction had produced compound **22**.

(13) Hall, L. D. In "The Carbohydrates"; Pigman, W., Horton, D., Eds.; Academic Press: New York, 1980; Vol IB, p 1304.

Table I. ^{1}H NMR Spectral Data[a]

compd	H-1	H-2	H-3	H-4	H-5	H-6	additional absorptions
18[b]	4.85 ($J_{1,2}$ = 3.6)	5.00 ($J_{2,3}$ = 8.0)	4.58 ($J_{3,4}$ = 5.7)	4.08	4.08 ($J_{5,6}$ = 6.6)	1.37	3.37 (OMe); 1.23 (CMe_3); 7.48–7.24 (C_6H_5); 6.13 (CHC_6H_5)
19[b]	4.80 ($J_{1,2}$ = 3.6)	4.91 ($J_{2,3}$ = 7.5)	4.48 ($J_{3,4}$ = 5.8)	4.10 ($J_{4,5}$ = 2.2)	3.80 ($J_{5,6}$ = 6.6)	1.41	3.37 (OMe); 1.23 (CMe_3); 7.60–7.35 (C_6H_5); 5.85 (CHC_6H_5)
20	4.95 ($J_{1,2}$ = 0)	4.14 ($J_{2,3}$ = 5.3)	4.47 ($J_{3,4}$ = 7.7)	5.01 ($J_{4,5}$ = 9.8)	3.80 ($J_{5,6}$ = 6.4)	1.23	3.38 (OMe); 1.23 (CMe_3); 7.25–7.45 (C_6H_5); 6.18 (CHC_6H_5)
21	5.00 ($J_{1,2}$ = 0)	4.22 ($J_{2,3}$ = 6.1)	4.33 ($J_{3,4}$ = 6.9)	4.94 ($J_{4,5}$ = 9.8)	3.74 ($J_{5,6}$ = 6.4)	1.19	3.38 (OMe); 1.23 (CMe_3); 7.35–7.55 (C_6H_5); 5.87 (CHC_6H_5)
22	4.97 ($J_{1,2}$ = 4.1)	5.07 ($J_{2,3}$ = 10.3)	4.31 ($J_{3,4}$ = 3.7)	5.50 ($J_{4,5}$ = 1.2)	4.18 ($J_{5,6}$ = 7.2)	1.21	3.40 (OMe); 1.23 (CMe_3); 8.18–8.06 (C_6H_5); 7.60–7.43 (C_6H_5)
23	4.79 ($J_{1,2}$ = 1.6)	5.32 ($J_{2,3}$ = 3.5)	4.13 ($J_{3,4}$ = 9.8)	5.03 ($J_{4,5}$ = 9.6)	3.87 ($J_{5,6}$ = 6.0)	1.24	3.39 (OMe); 1.24 (CMe_3); 8.17–7.93 (C_6H_5); 7.60–7.13 (C_6H_5)

[a] Chemical shifts are in parts per million from Me_4Si. Coupling constants are in Hertz. [b] Chemical shifts for H-2, H-3, H-4, H-5 and coupling constants $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ were obtained by spectral simulation.

Table II. ^{13}C NMR Spectral Data[a]

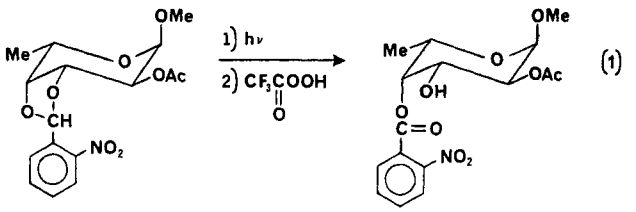
	18	19	20	21	22	23
C-1	97.25	97.22	98.31	98.98	97.66	98.60
C-2, C-3, C-4	76.24	78.39	77.37	78.05	74.39	74.79
	74.88	73.39	75.75	75.73	71.49	73.38
	68.99	72.18	71.39	74.79	67.34	69.06
C-5	63.18	63.06	63.75	63.92	64.97	66.13
C-6	16.42	16.21	17.12	17.18	16.29	17.53
OCH_3	55.59	55.59	55.06	54.94	55.65	55.20
Me_3C	38.81	38.80	38.86	38.79	38.92	39.01
Me_3C	27.09	27.09	27.16	27.00	27.04	27.12
C_6H_5CH	102.90	104.31	103.17	104.67		
C_6H_5 *i*	139.19	137.34	138.62	136.67	129.59	129.68
o,m	128.34	128.37	128.41	128.41	129.99	129.93
	126.29	128.86	126.38	127.07	128.51	128.53
p	129.01	129.35	129.21	129.51	133.31	133.39
$Me_3CC(O)$	177.29	177.0	177.56	177.20	178.76	179.03
$C_6H_5C(O)$					166.71	166.39

[a] Chemical shifts are in parts per million from Me_4Si.

A similar, light-initiated reaction was conducted between NBS, water, and the L-rhamnose derivatives **20** and **21**. Ring opening occurred (75% yield) in the expected manner to place an axial benzoyloxy group on C-2 and leave an equatorial hydroxy on C-3. The structure of the reaction product (**23**) was established by a combination of spectral (Tables I and II) and chemical evidence (see Experimental Section) in a manner similar to that described above for compound **22**.

The chemistry of benzylidene acetals of carbohydrates has recently been thoroughly reviewed.[14] Various methods for ring opening to produce partially protected carbohydrates have been discussed and carefully analyzed. In light of what is known about reactions of these compounds, several aspects of the ring-opening process described here deserve special emphasis. First, the reaction under consideration here produces only the thermodynamically less stable, ring-open product, that is, the isomer with axial benzoyloxy and equatorial hydroxy groups. This reaction, therefore, complements thermodynamically controlled, ring-opening reactions. Also, in the photochemically initiated process the same ring-open product is formed regardless of whether the phenyl group in the benzylidene acetal is exo or endo to the pyranose ring; thus, there is no need to separate diastereomeric pairs (**4** and **5**, **18** and **19**, or **20** and **21**) prior to ring opening. In addition, rearrangements or other side reactions are not significant for the compounds studied. This fact may be attributed, at least in part, to the mild conditions (room temperature, inert solvent (CCl_4), and rapid neutralization of any acid formed) under which reaction is conducted. This combination of advantages suggests that the reaction described here could be useful in a number of situations.

Finally, it is of particular interest to compare the light-initiated, NBS reaction described here with the photolysis of *o*-nitrobenzylidene acetals,[15] another method for partial deprotection of carbohydrates. The essential molecular change produced by these two reactions is similar but the ease of conduct of the experiments is different. The NBS reaction has several advantages. The reagents used to prepare benzylidene acetals (benzaldehyde, α,α-dimethoxytoluene, etc.) are more readily available (and much less costly) than the corresponding reagents used to synthesize *o*-nitrobenzylidene acetals. The NBS reaction is a one-step process while *o*-nitrobenzylidene acetal photolysis requires treatment of the photoproduct with trifluoroperacetic acid to obtain a characterizable product (eq 1).[15b] Lastly, benzylidene acetals are used widely as



(1)

protecting groups in carbohydrate chemistry; consequently, many of the compounds for which partial deprotection using the NBS reaction would be valuable already have been prepared and characterized. In contrast, the *o*-nitrobenzylidene group is rarely used to protect carbohydrates.

Experimental Section

General Procedures. ^1H NMR spectra were run on Varian T-60 and FT-80A spectrometers. The ^{13}C NMR spectra were obtained from a Varian FT-80A spectrometer. Spectral simulation was done with the Varian Associates Simeq spin simulation program. Preparative Liquid Chromatography was conducted by using a Waters Prep LC/SYSTEM 500A.

Synthesis of Methyl 2,4-Di-*O*-benzoyl-β-L-arabinopyranoside (10). Methyl 2-*O*-benzoyl-3,4-*O*-(*S*)-benzylidene-β-L-arabinopyranoside[16] (**4**, 1.14 g, 3.2 mmol) was dissolved in 200 mL of CCl_4. Barium carbonate (5.0 g), *N*-bromosuccinimide (0.95 g, 5.3 mmol), and water (0.25 g, 13.9 mmol) were added to the vigorously stirred reaction mixture. The reaction mixture was then irradiated (stirring continued) for 2.5 h with a Nester-Faust, low-pressure, mercury-vapor lamp. (TLC indicated complete reaction.) The reaction mixture was filtered and the solvent was distilled under reduced pressure. The residue was dissolved in 200 mL of ethyl ether and washed with 100 mL of water. The ether solution was dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was chromatographed on a 2.5 × 15 cm column of 230–400 mesh silica gel using 1:2 ether–hexane as the eluent; 20 mL fractions were collected. Only fractions 18–26 contained significant amounts of material. Upon solvent removal, the product crystallized. TLC analysis showed only one spot. The product was recrystallized from ethyl acetate–hexane to give 0.73 g (62% yield) of 2,4-di-*O*-benzoyl-β-L-arabinopyranoside: mp 153–154 °C (lit.[17] 147–149 °C); ^1H NMR ($CDCl_3$) δ 8.0–7.4, 5.38 (H-4, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 2.0 Hz), 5.37 (H-2, $J_{1,2}$ = 3.4 Hz, $J_{2,3}$ = 9.5 Hz), 5.05 (H-1), 4.40 (H-3), 3.90 (H-5, H-5′, $J_{4,5}$ = 2.0 Hz, $J_{4,5'}$ = 2.0 Hz), 3.40 (OCH_3), 2.8 (OH). (The coupling constants

(14) Gelas, J. *Adv. Carbohydr. Chem. Biochem.* **1981**, *39*, 71.
(15) (a) Collins, P. M.; Munasinghe, V. R. N. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1879 and references cited therein. (b) Collins, P. M.; Oparaeche, N. N. *Ibid.* **1975**, 1695.
(16) Clode, D. M. *Can. J. Chem.* **1977**, *55*, 4066.
(17) Abbas, S. A.; Haines, A. H.; Wells, A. G. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1351.

and chemical shifts for this compound were confirmed by simulation of the portion of the spectrum due to protons attached to the pyranose ring.) This spectrum is the same as that reported for the enantiomer of the 2,4-dibenzoate **10** and different from that for the enantiomer of the 2,3-dibenzoate **11**.[18] ^{13}C NMR ($CDCl_3$) δ 166.9 (CO), 166.4 (CO), 133.4, 129.9, 129.6, 128.4 (aromatic), 80.0 (C-1), 72.7, 72.4, 66.7 (C-2, C-3, C-4), 60.4 (C-5), 55.7 (OCH_3).

Methyl 2-*O*-benzoyl-3,4-*O*-(*R*)-benzylidene-β-L-arabinopyranoside[16] **(5)** was treated in the same manner as its diastereomer **4** and provided an identical result.

Synthesis of Methyl 6-Deoxy-α-L-galactopyranoside (Methyl α-L-Fucopyranoside, 12) and 6-Deoxy-α-L-mannopyranoside (Methyl α-L-Rhamnopyranoside, 13). L-Rhamnose monohydrate **(3)** (100 g, 0.55 mmol) and the acid catalyst Dowex 50W-X8 were combined with 500 mL of CH_3OH and refluxed for 48 h. The reaction mixture was cooled, filtered, and concentrated under vacuum using a water aspirator. Additional solvent was removed by a mechanical pump. The residue solidified and was crystallized from ethyl acetate to give 38 g of methyl α-L-rhamnopyranoside **(13)**: mp 108–109 °C (lit.[19] 109–110 °C). The filtrate, after crystallization, was concentrated and 500 mL of methanol was added. The ion exchange resin was returned to the reaction mixture and the reflux and isolation process was repeated twice to give an additional 31 g and 27 g, respectively, of methyl α-L-rhamnopyranoside **(13)** with a total yield of 96 g (90%).

A similar process was used to convert L-fucose **(2)** (25 g, 0.150 mol) into methyl α-L-fucopyranoside **(12)** (24.2 g, 0.136 mol, 91%): mp 156–158 °C (lit.[20] 157.5–158.5 °C).

Synthesis of Methyl 3,4-*O*-Benzylidene-(*S* and *R*)-6-deoxy-α-L-galactopyranoside (14 and 15) and Methyl 2,3-*O*-Benzylidene-(*S* and *R*)-6-deoxy-α-L-mannopyranoside (16 and 17). Compounds **14** and **15** were prepared from **2** according to the method of Bundle and Josephson[21] while **16** and **17** were synthesized from methyl α-L-rhamnopyranoside **(3)** according to the procedure of Liptak and co-workers.[22]

Synthesis of the Esters 18–21. A general procedure for esterification of compounds **18–21** is described here. Anhydrous pyridine (200 mL) and 7.5 g (2.82×10^{-2} mol) of the protected sugar **(14–17)** were combined and stirred until solution was complete. Pivaloyl chloride (5.62 g, 5.75 mL, 5.0×10^{-2} mol) was added dropwise to this solution which was stirred rapidly and maintained at 25 °C. After the addition was complete, the reaction mixture was allowed to stand overnight at room temperature. The crystalline material that formed upon standing dissolved upon the dropwise addition of 5 mL of H_2O to the stirred solution. The reaction mixture was stirred for 4 h and then concentrated under reduced pressure to yield a residue which was partitioned between CCl_4 (350 mL) and saturated $NaHCO_3$ (250 mL). The aqueous layer was extracted twice (250 mL) with CCl_4 and the combined organic extracts, after removal of all volatile material, were passed through a short (2.50 × 10 cm) column of silica gel using ethyl acetate–toluene (1:10) to remove the color. Although each of the compounds was homogeneous by TLC, only one **(20)** crystallized (from hexane), mp 102.5–105 °C. The reactions were quantitative. The ^1H and ^{13}C NMR spectra are given in Tables I and II. Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.16; H, 7.44. Found: C, 65.11; H, 7.45 (compound **18**); C, 65.31, H, 7.51 (compound **19**); C, 65.11; H, 7.41 (compound **20**); C, 65.25; H, 7.36 (compound **21**).

Direct Synthesis of the Esters 18–21. A mixture of the esters **18** and **19**, suitable for further reaction, was prepared most easily from methyl 6-deoxy-α-L-galactopyranoside **(12)** without isolation of the intermediates **14** and **15**. Preparation of a mixture of **20** and **21** from **13** also was done most efficiently without isolation of intermediates **16** and **17**. The benzylidene acetals **14** and **15** (or **16** and **17**) were prepared by the procedure of Evans[12] by heating **12** (or **13**) with α,α-dimethoxytoluene in *N,N*-dimethylformamide. (A simple procedure for removing any water from the reaction mixture before addition of the α,α-dimethoxytoluene was to double the amount of DMF added and then distill the DMF and any water present from the sugar solution until a constant temperature was reached.) Once the solution had cooled, it was combined directly with anhydrous pyridine and esterified as described above. Chromatography of the reaction mixture was unnecessary if only the hexane soluble material, extracted from the residue after complete solvent removal, was used. Distillation of the hexane left a yellow oil which was suitable for reaction with *N*-bromosuccinimide (NBS).

Synthesis of Methyl 4-*O*-Benzoyl-6-deoxy-2-*O*-(2,2-dimethylpropanoyl)-α-L-galactopyranoside (22) and Methyl 2-*O*-Benzoyl-6-deoxy-4-*O*-(2,2-dimethylpropanoyl)-α-L-mannopyranoside (23). A typical procedure is described. This procedure was used on the pure esters **18–21** as well as mixtures of **18** with **19** and **20** with **21**. Carbon tetrachloride (400 mL), NBS (3.33 g, 1.85×10^{-2} mol), water (30 mL), and 5.88 g (1.68×10^{-2} mol) of compound **20** were combined, purged with N_2 for 1 h, and stirred vigorously while being irradiated with either (a) a 300-W sun lamp for two days, (b) a Nester-Faust, low-pressure, mercury-vapor lamp for 6 h, or (c) a Pyrex-filtered, 450-W Hanovia, mercury-vapor lamp for 30 min. The reaction mixture was filtered and the residue washed with 200 mL of CCl_4. The solvent was distilled and the residue extracted with hexane. The hexane was distilled and the reaction mixture crystallized. This material was recrystallized from ethyl acetate–hexane (1:1) to give 4.9 g (72%) of 4-*O*-benzoyl-6-deoxy-2-*O*-(2,2-dimethylpropanoyl)-α-L-galactopyranoside **(22)**, mp 133–134 °C (from ethyl acetate). ^1H and ^{13}C NMR spectra are given in Tables I and II. Anal. Calcd for $C_{19}H_{26}O_7$: C, 62.28; H, 7.15. Found: C, 62.48; H, 7.15.

The synthesis of 2-*O*-benzoyl-4-O-(2,2-dimethylpropanoyl)-α-L-rhamnopyranoside **(23)** was conducted in the same manner; however, this material failed to crystallize. Since TLC showed several minor impurities, a sample of this material (19 g) was chromatographed on silica using a Waters Prep LC/SYSTEM 500A and ethyl acetate–toluene (1:7) as the solvent. This gave 18.2 g of a material which was homogeneous by TLC and gave the expected ^1H and ^{13}C NMR spectra but did not crystallize. Anal. Calcd for $C_{19}H_{26}O_7$: C, 62.28; H, 7.15. Found: C, 62.38; H, 7.03.

Methanolysis of Compounds 22 and 23. The esters **22** and **23** each were dissolved in methanol, Baker ANGA-542 ion exchange resin was added, and the mixtures were refluxed for 2 h. The reaction mixtures were filtered and the solvent distilled. Compound **22** produced methyl α-L-fucopyranoside **(12)** and compound **23** formed m ethyl α-L-rhamnopyranoside **(13)**.

Registry No. **2**, 2438-80-4; **3**, 3615-41-6; **4**, 65914-27-4; **5**, 65914-29-6; **10**, 60551-04-4; **12**, 14687-15-1; **13**, 14917-55-6; **14**, 69349-72-0; **15**, 69349-73-1; **16**, 65529-46-6; **17**, 65529-48-8; **18**, 88825-53-0; **19**, 88825-54-1; **20**, 88825-55-2; **21**, 88825-56-3; **22**, 88825-51-8; **23**, 88825-52-9.

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