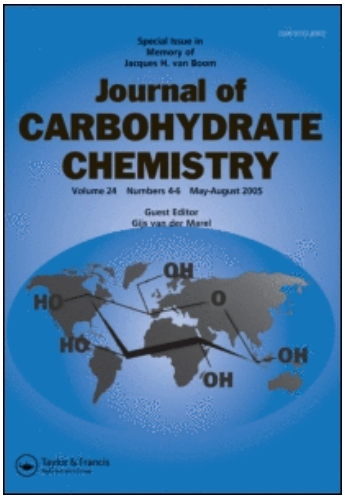

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Participation by C-3 Substituents in Disaccharide Formation

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To cite this Article Binkley, Roger W. and Koholic, Dolores J.(1988) 'Participation by C-3 Substituents in Disaccharide Formation', Journal of Carbohydrate Chemistry, 7: 2, 487 — 499
To link to this Article: DOI: 10.1080/07328308808058937
URL: http://dx.doi.org/10.1080/07328308808058937

J. CARBOHYDRATE CHEMISTRY, 7(2), 487-499 (1988)

PARTICIPATION BY C-3 SUBSTITUENTS IN DISACCHARIDE FORMATION

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Received December 8, 1987 - Final Form February 25, 1988

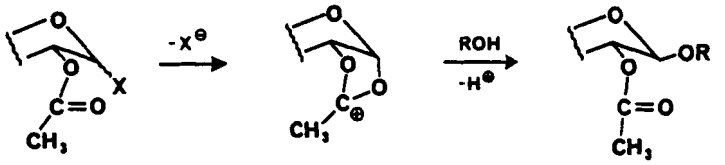
ABSTRACT

Four reactions were conducted in order to study the ability of a C-3 acyloxy group to control the stereoselectivity of glycosidation reactions in which the glycosyl donors were unsubstituted at C-2. These donors differed in the structure of the acyloxy group attached to C-3 (benzoyloxy or *p*-methoxybenzoyloxy) and in the identity of the leaving group (chloro or thiomethoxy) attached to the anomeric carbon. The stereoselectivity in all reactions was low; for example, treatment of 3,4-di-*O*-benzoyl-2,6-dideoxy-D-ribo-hexopyranosyl chloride (6) with methyl 4-*O*-benzoyl-2,6-dideoxy-α-D-*lyxo*-hexopyranoside (7) yielded a 2.2/1 (α/β) ratio of methyl 4-*O*-benzoyl-3-*O*-(3,4-di-*O*-benzoyl-2,6-dideoxy-α-D-*ribo*-hexopyranosyl)-2,6-dideoxy-α-D-*lyxo*-hexopyranoside (8) and methyl 4-*O*-benzoyl-3-*O*-(3,4-di-*O*-benzoyl-2,6-dideoxy-β-D-*ribo*-hexopyranosyl)-2,6-dideoxy-α-D-*lyxo*-hexopyranoside (9). Formation of 1,5-anhydro-3,4-di-*O*-benzoyl-2,6-dideoxy-D-*ribo*-hex-1-enitol (10) was a significant additional reaction. In reactions involving the thioglycosides only trace amounts of glycals were formed and approximately equal amounts of α and β anomers were produced. The significance of these reactions to participation by C-3 acyloxy groups is discussed.

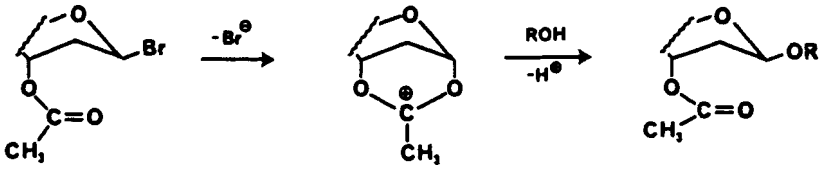
INTRODUCTION

Stereoselectivity in the synthesis of β-glycosidic linkages between pyranoid ring systems is most easily achieved when a properly positioned C-2 substituent directs glycoside formation (Scheme I). If there is no functional group attached to C-2 or if the C-2 substituent does

Scheme I

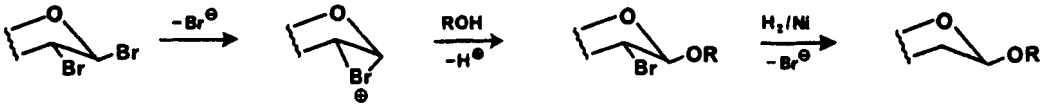


Scheme II



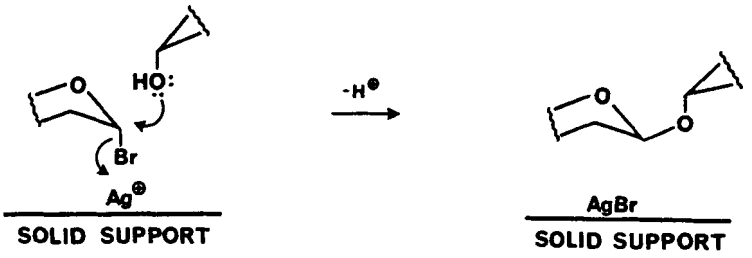
not participate in the reaction, β-glycoside formation still can be realized through other means. One of these is by participation of a group attached to another carbon atom (Scheme II). A second is through use of a temporary participating group which is removed after glycoside formation (Scheme III). Third and most often employed is a method for

Scheme III

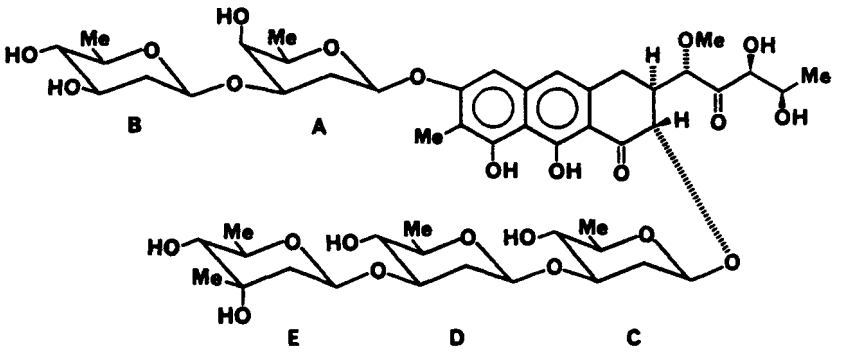


β-glycoside synthesis which does not depend on group participation but rather on a combination of an α-glycosyl halide reacting with a partially protected sugar under conditions which promote reaction on the β-face of the halide (Scheme IV). In this latter approach selection of the reaction catalyst (an insoluble silver-ion containing salt) is critical. The choice is almost always between silver silicate, first used by Paulsen and coworkers,[1,2] or silver zeolite, introduced by Garegg and Ossowski.[3]

Scheme IV



The need to form β-glycosidic linkages without the benefit of normal C-2 participation is no where more apparent than in the synthesis of the carbohydrate portions of mithramycin (1), an antitumor agent with five beta-linked sugar residues but no C-2 substituents. Thiem and coworkers have been studying the synthesis of this compound (1) for several years[4,5] and recently have reported formation of the most challenging saccharide unit in the molecule, the C-D-E trisaccharide.[6] Their synthetic work has been characterized by effective use of bromine as a temporary participating group for directing β-glycoside formation.[7]



1

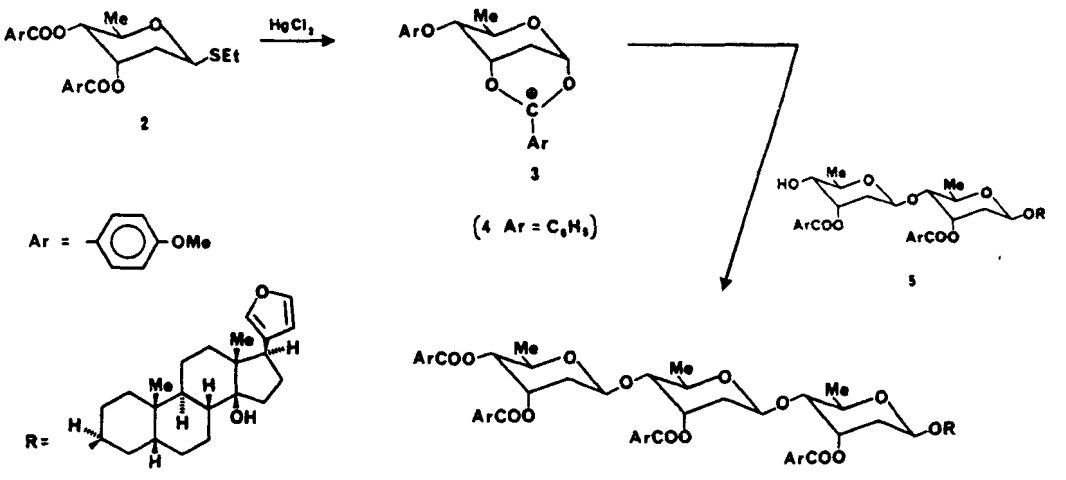
Our interest in formation of β-glycosides arises from a desire to synthesize carbohydrate modified analogs of mithramycin (1). The structure of the carbohydrates in these analogs is such that synthetic

approaches other than bromine participation needed to be considered. One of these approaches was participation by a group attached to C-3. The recent success experienced by Wiesner and coworkers[8,9] with 3-O-*p*-methoxybenzoyl participation in glycoside formation (Scheme V) indicated that this approach might also be used to direct the oligosaccharide synthesis involved in mithramycin analog preparation. (Recently we reported a procedure for obtaining 2,6-dideoxy-D-*ribo*-hexopyranosyl derivatives from digitoxin.[10] These derivatives represented a convenient source of starting materials with C-3 participating groups properly positioned to direct β-glycoside synthesis.)

RESULTS AND DISCUSSION

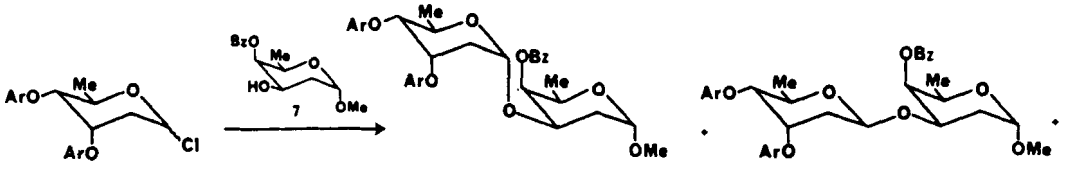
Reaction of 3,4-di-*O*-benzoyl-2,6-dideoxy-D-*ribo*-hexopyranosyl chloride (6) with methyl 4-*O*-benzoyl-2,6-dideoxy-α-D-*lyxo*-hexopyranoside (7) in dichloromethane in the presence of 2,6-di-*tert*-butyl-4-methylpyridine gave the disaccharides 8 and 9 (Equation 1), in 41 and 19% yields, respectively; thus, the ratio of α/β anomers was 2.2/1. Also produced during this reaction was 1,5-anhydro-3,4-di-*O*-benzoyl-2,6-

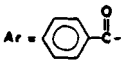
Scheme V

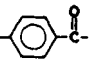


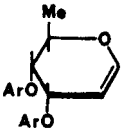
dideoxy-D-*ribo*-hex-1-enitol (**10**) in 35% yield. The stereochemistry at C-1' in compounds **8** and **9** was determined from the coupling constants between H-1' and the hydrogens attached to C-2' ($J_{1',2a'} = J_{1',2e'} < 1$ Hz for **8** while $J_{1',2a'} = 9.2$ Hz and $J_{1',2e'} = 1.8$ Hz for **9**).

Although the α-glycoside **8** was the major product from this reaction, the ratio of **8**/**9** was somewhat smaller than that expected from halide catalyzed reaction. (Halide catalyzed glycosidation probably was taking place once reaction had begun and chloride ion was present.) Since any 3-*O*-benzoyl participation in this reaction would be expected to reduce the α/β ratio, some involvement of the benzoyl group may have occurred; however, if participation was taking place, its influence on the reaction was too small to be useful in synthesizing mithramycin analogs. In addition, other problems with this reaction existed. The rate was slow (three days required for completion) and the amount of elimination product (**10**) (35% yield) was considerable.

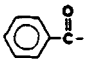


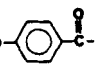
6 Ar =  **8** **9**

13 Ar = MeO-  **14** **15**



(Eq. 1)

16 Ar = 

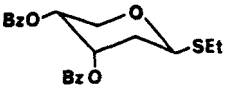
16 Ar = MeO- 

Addition of a catalyst could be expected to increase the reaction rate but its effect on the ratio of 8/9 and on the amount of 10 produced was uncertain. Several catalysts were tested. Reaction in the presence of silver silicate did reduce the reaction time to several hours but it did not increase participation by the C-3 benzoyloxy group. (The observed of 8/9 ratio from this reaction was 3/1.) Silver zeolite had a similar effect. Conducting the reaction in the presence of tetrabutylammonium bromide also increased the rate and the amount of elimination. The reactions in the presence of these several catalysts indicated that changes in reactant structure or reaction conditions needed be considered.

The identity of the leaving group at C-1 and the nature of the participating group at C-3 were two elements in the structure of the glycosyl halide 6 for which change might significantly alter the ratio of anomers formed from reaction with 7. The participating group was altered first. The *p*-methoxybenzoyl group, which had been selected for participation by Wiesner and coworkers,[8,9] forms a more stable bridged ion (3) than that derived from an unsubstituted benzoyl group (4) (Scheme V); thus, *p*- methoxybenzoyl participation should occur more easily than benzoyl involvement and, as a result, more β-glycoside should be formed. Reacting compound 7 with 2,6-dideoxy-3,4-di-*O*-(*p*-methoxybenzoyl)-D-*ribo*-hexopyranosyl chloride (13) did change the α/β ratio to 1.4/1 in the disaccharides formed (14 and 15) but substantially more elimination reaction occurred than when the dibenzoyl glycosyl halide 6 was used (Equation 1).

If the elimination process in these reactions were taking place, at least in part, directly from the α-anomers of 6 and 13 but not from the bridged ions (3 and 4), using a β-thioglycoside as the glycosylating agent could substantially reduce the amount of elimination reaction. When compound 7 reacted with ethyl 3,4-di-*O*-benzoyl-2,6-dideoxy-1-thio-β-D-*ribo*-hexopyranoside (17) in the presence of mercury(II) chloride, only traces of the glycal 10 were formed while the disaccharides 8 and 9 were produced in a ratio of 1.1/1 (Equation 2). Using the di-*O*-*p*-methoxybenzoyl thioglycoside 2 in place of 17 also reduced the amount of elimination reaction and slightly improved the α/β ratio (1/1) in the disaccharides formed (Equation 3).

Although using the *p*-methoxybenzoyl protected thioglycoside 2 provided the best result in terms of β-glycoside syntheses (Equation 3), preference for β-anomer formation in the reaction between 2 and 7 did not approach that of the reaction shown in Scheme V. (In the reaction pictured in Scheme V a small amount of α anomer also was formed, giving rise to an α/β ratio of anomers of 1/25.) The difference in stereoselectivity between the reaction shown in Scheme V and that in Equation 3 probably is attributable to the greater reactivity of the C-3 hydroxyl group in compound 7 when compared to the hydroxyl group at C-4 in compound 5. Increased reactivity would be expected to result in a reduction of stereoselectivity; however, the magnitude of the change is greater than was anticipated.



17

$$17 + 7 \xrightarrow{HgCl_2} 8 + 9 \qquad \text{(Eq. 2)}$$

$$2 + 7 \longrightarrow 15 + 16 \qquad \text{(Eq. 3)}$$

In conclusion, the results from this study indicate that although group participation appears to be taking place in formation of the disaccharide 8, 9, 14, and 15, it is not the dominating factor characteristic of glycosyl donors with acyloxy groups attached to C-2. The relatively large separation between the leaving group (at C-1) and the participating group (at C-3) in the glycosyl donor reduces the opportunity for interaction.

EXPERIMENTAL

General Procedures. TLC was conducted using Whatman MK6F silica gel plates. The solvent mixture used for TLC and column chromatography consisted of hexane and ethyl acetate (3/1), unless otherwise noted. Column chromatography was done on a 2.5 x 15 cm column of 230-400 mesh silica gel. The molecular sieves used were 3A and were

activated prior to use by heating for 20 h at 250 °C. NMR spectra ($CDCl_3$) were determined using a Varian FT80A spectrometer, except were noted. Spectral data are given in Tables 1 and 2. Optical rotations were determined for solutions in chloroform at 22 °C using a Perkin Elmer model 141 spectrometer.

Synthesis of Methyl 4-*O*-Benzoyl-3-*O*-(3,4-di-*O*-benzoyl-2,6-dideoxy-α-D-*ribo*-hexopyranosyl)-2,6-dideoxy-α-D-*lyxo*-hexopyranoside (8) and Methyl 4-*O*-Benzoyl-3-*O*-(3,4-di-*O*-benzoyl-2,6-dideoxy-β-D-*ribo*-hexopyranosyl)-2,6-dideoxy-α-D-*lyxo*-hexopyranoside (9).

a. From the Glycosyl Halide 6. Freshly prepared 3,4-di-*O*-benzoyl-2,6-dideoxy-D-*ribo*-hexopyranosyl chloride[10] (6) (0.60 g, 1.6 mmol), methyl 4-*O*-benzoyl-2,6-dideoxy-α-D-*lyxo*-hexopyranoside[11] (7) (0.40 g, 1.5 mmol), and 2,6-di-*tert*-butyl-4-methylpyridine (0.61 g, 3.0 mmol) were dissolved in 10 mL of anhydrous toluene and allowed to stand at room temperature. The reaction mixture was monitored by TLC. Glycoside formation was complete after three days. The reaction mixture was chromatographed in the standard fashion to give four significant fractions. The first (R_f 0.54) contained 0.18 g (0.53 mmol, 35%) of 1,5-anhydro-3,4-di-*O*-benzoyl-2,6-dideoxy-D-*ribo*-hex-1-enitol (10), mp 53-55 °C, [α] +415° (c 0.44). Anal. Calcd for $C_{20}H_{18}O_5$: C, 70.99; H, 5.36. Found C, 70.98; H, 5.45. The second compound eluted from the column (0.18 g, 0.29 mmol, R_f 0.35) was methyl 4-*O*-benzoyl-3-*O*-(3,4-di-*O*-benzoyl-2,6-dideoxy-β-D-*ribo*-hexopyranosyl)-2,6-dideoxy-α-D-*lyxo*-hexopyranoside (9), a liquid, $[\alpha]_D$ +127° (c 0.54). Anal. Calcd for $C_{34}H_{36}O_{10}$: C, 67.54; H, 6.00. Found: C, 67.65; H, 6.13. The third fraction contained 0.37 g (0.62 mmol, 41%) of methyl 4-*O*-benzoyl-3-*O*-(3,4-di-*O*-benzoyl-2,6-dideoxy-α-D-*ribo*-hexopyranosyl)-2,6-dideoxy-α-D-*lyxo*-hexopyranoside (8), a liquid (R_f 0.54, $[\alpha]_D$ +127° (c 0.63). Anal. Calcd for $C_{34}H_{36}O_{10}$: C, 67.54; H, 6.00. Found: C, 67.55; H, 6.18. The ^1H NMR[11] and ^{13}C NMR spectra of compounds 8 and 9 are given in tabular from in Tables 1 and 2, respectively. The final fraction contained 0.15 g of unreacted 7.

Additional reactions between compounds 6 and 7 were conducted in the presence of silver silicate (1 g), silver zeolite (1 g), and tetrabutylammonium bromide (0.25 g), respectively. Except for the addition of one of these catalysts, the reaction and isolation conditions were the same as those described above. The products and yields were (a) from

TABLE 1. ^{1}H NMR SPECTRAL DATA

CHEMICAL SHIFTS[a]

	8	9	10	11	13	14	15	16
H-1	4.80	4.73	6.58	6.45	6.26	4.77	4.73	6.58
H-2a	1.80-	2.28	5.07	2.34-	2.43-	1.80-	2.05	5.05
H-2e	2.40	2.05		2.50	2.68	2.40	2.26	
H-3	4.45	4.48	5.80	5.88	5.76	4.45	4.48	3.74
H-4	5.21	5.76	5.28	5.10	5.04	5.20	5.71	5.23
H-5	3.69	3.83	4.47	4.45	4.76	3.69	3.83	4.44
H-6	1.11	1.36	1.38	1.39	1.31	1.20	1.36	1.39
H-1'	5.35	5.12				5.35	5.12	
H-2a'	1.80	1.67				1.80-	1.66	
H-2e'	2.40-	1.93				2.40	1.92	
H-3'	5.68	5.78				5.64	5.73	
H-4'	5.12	4.99				5.09	4.99	
H-5'	4.63	4.21				4.61	4.18	
H-6'	1.24	1.25				1.26	1.25	
OMe	3.39	3.39				3.39	3.39	
ArOMe				3.87	3.86	3.84	3.87	3.80
ArOMe				3.78	3.81	3.78	3.78	3.75
ArH	8.10-	8.33-	8.06-	8.07-	8.17-	8.10-	8.07-	8.02-
"	7.99	7.95	7.86	7.73	7.79	7.99	7.73	7.81
"	7.16-	7.16-	7.53-	7.54-	7.00-	7.16-	7.50-	6.93-
"	6.88	6.86	7.19	7.24	6.76	6.88	7.21	6.73
				6.98-		6.73-	6.98-	
				6.71		6.61	6.71	

COUPLING CONSTANTS[b]

1,2a	2.50	2.60	5.90	7.40	2.60	2.50	2.60	5.90
1,2e	c	c		3.90	2.60	c	c	
2a,3	12.00	12.00	5.50	3.20	3.00	12.00	12.00	5.80
2e,3	5.00	4.60		3.20	3.00	5.00	4.60	
3,4	3.00	2.30	3.90	3.20	3.00	4.00	3.20	3.90
4,5	c	c	10.30	9.40	10.40	c	c	10.30
5,6	6.40	6.50	6.30	6.50	6.00	6.40	6.50	6.30
1,2a'	c	9.20				c	9.20	
1,2e'	c	1.80				c	1.80	
2a',3'	3.30	3.10				3.30	3.00	
2e',3'	3.30	3.10				3.30	3.00	
3',4'	3.30	3.10				3.10	2.90	
4',5'	9.70	9.60				9.70	9.50	
5',6'	6.50	6.20				6.50	6.20	

[a]Chemical shifts are relative to Me_4Si. Atoms in *ribo* residue are indicated by a prime (') mark. [b]Coupling constants are in Hertz. [c]Coupling constant is less than 1 Hz.

TABLE 2. ^{13}C NMR SPECTRAL DATA[a]

	8	9	10	11	12α	12β	14	15	16
C-1	98.89	98.89	148.27	91.31	90.59	92.43	98.96	98.95	148.09
C-2	31.99	31.17	97.68	34.40	33.90	37.03	32.10	31.16	97.84
C-3	67.78	70.88	71.91	70.31	67.16	68.65	67.93	70.80	71.57
C-4	69.17	72.39	69.67	72.28	72.28	72.44	69.35	72.41	69.67
C-5	64.75	65.58	64.07	67.38	62.43	67.93	64.88	65.62	63.69
C-6	16.90	17.03	117.27	18.31	17.45	17.87	16.93	16.91	17.26
C-1'	93.12	96.30					93.32	96.64	
C-2'	33.33	36.08					33.46	36.10	
C-3'	66.93	68.60					66.72	68.73	
C-4'	73.07	73.05					72.83	72.80	
C-5'	62.55	68.60					62.77	68.37	
C-6'	17.71	18.01					17.73	17.99	
OMe	54.89	54.90					54.89	54.89	
ArOMe				55.47	55.24	55.24	55.41	55.39	55.39
ArOMe				55.47	55.24	55.24	55.41	55.45	55.39
ArOMe				55.47					
C=O	166.57	165.40	165.90	165.23	165.04	165.04	165.25	165.25	165.60
C=O	165.49	165.40	165.35	165.16	164.89	164.89	165.25	165.25	165.01
C=O				164.59					
Ar	133.06	133.21	133.23	163.92	163.39	163.39	163.57	163.57	163.64
"	132.81	132.90	133.00	163.67	163.33	163.33	163.57	163.57	163.49
"	129.90	132.79	129.75	132.14	131.50	131.50	132.79	133.19	131.77
"	129.66	129.86	129.68	131.81	122.11	122.11	131.74	131.71	131.67
"	128.28	129.64	128.38	122.26	121.69	121.69	131.68	129.90	122.69
"	127.98	128.52		121.78	113.57	113.57	129.62	128.46	121.92
"		128.31		113.78	113.40	113.40	128.26	113.83	113.66
"							113.65	113.65	113.66
"							113.34		

[a]Chemical shifts are relative to Me_4Si. Atoms in *ribo* residue are indicated by a prime (') mark.

the silver silicate catalyzed reaction 8 (12%), 9 (4%), and 10 (64%); (b) from the silver zeolite reaction 8 (11%), 9 (4%), and 10 (80%); and (c) from the tetrabutylammonium bromide reaction 8 (7%), 9 (3%), and 10 (80%).

b. From the Thioglycoside 17. Compound 7 (0.12 g, 0.45 mmol), the thioglycoside 17[10] (0.23 g, 0.54 mmol), and 0.20 g (0.98 mmol) of 2,6-di-*tert*-butyl-4-methylpyridine were dissolved in 10 mL of dry dichloromethane and stored overnight over 1 g of 3A molecular sieves. The solution was filtered and 0.75 g of mercury(II) chloride was added to

the stirred reaction mixture. After stirring overnight, the reaction mixture was filtered, concentrated, and chromatographed in the standard fashion. The products formed were compounds 8 (0.13 g, 0.22 mmol, 48%) and 9 (0.12 g, 0.19 mmol, 41%).

Synthesis of 2,6-Dideoxy-1,3,4-tri-*O*-(*p*-methoxybenzoyl)-β-D-*ribo*-hexopyranose (11). Digitoxose[10] (2.87 g, 19.4 mmol) was dissolved in 100 mL of anhydrous pyridine, cooled in an ice bath, and 14.9 g (87.3 mmol) of *p*-methoxybenzoyl chloride was added dropwise to the stirred solution. The reaction mixture was allowed to warm to room temperature and stand overnight. The reaction mixture was again placed in an ice bath and 10 mL of water was added dropwise with vigorous stirring. After 30 min, the reaction mixture was added slowly to a stirred solution of 40 g of sodium bicarbonate in 600 mL of water. The precipitate which formed was removed by filtration, washed with 100 mL of water, and recrystallized from ethanol to give 6.94 g (12.6 mmol, 65%) of 2,6-dideoxy-1,3,4-tri-*O*-(*p*-methoxybenzoyl)-β-D-*ribo*-hexopyranose (11), mp 151-153 °C, $[\alpha]_D$ +93° (c 0.33). Anal. Calcd for $C_{30}H_{30}O_{10}$: C, 65.44; H, 5.49. Found: C, 65.41; H, 5.40.

Synthesis of 2,6-Dideoxy-3,4-Di-*O*-(*p*-methoxybenzoyl)-D-*ribo*-hexopyranose (12).[8] Compound 11 (4.56 g, 8.30 mmol) was dissolved in a solution consisting of 50 mL of THF, 4 mL of water, and 1 mL of concentrated sulfuric acid. After standing at room temperature for 4 days, 10 g of sodium bicarbonate was added slowly with stirring and the solution was stirred until it was no longer acidic (litmus). The reaction mixture was partitioned between water (100 mL) and ether (150 mL) and the layers were separated. The aqueous layer was extracted with two 100 mL portions of ether and the ether extracts were passed through a 1 cm bed of silica gel (240-400 mesh). Distillation of the solvent left a material which was chromatographed under standard conditions to give 3.11 g (7.75 mmol, 90%) of 2,6-dideoxy-3,4-di-*O*-(*p*-methoxybenzoyl)-D-*ribo*-hexopyranose (12), mp 96-98 °C, $[\alpha]_D$ +195° (c 0.19). ^{13}C NMR analysis of this material indicated it to be a 3.5/1 (α/β) mixture of anomers.

Synthesis of 2,6-Dideoxy-3,4-Di-*O*-*p*-(methoxybenzoyl)-D-*ribo*-hexopyranosyl Chloride (13). Compound 12 (1.30 g, 3.00 mmol) was dissolved in 50 mL of anhydrous toluene. This solution was cooled to 0 °C

and anhydrous hydrogen chloride was bubbled into the stirred, cooled solution for 20 min. The solvent and the hydrogen chloride were removed under reduced pressure at room temperature. The product was an unstable material which reverted to compound **12** upon exposure to moisture or attempted chromatography. The ^{1}H NMR spectrum (Table 1) indicated the product to be a 5/1 mixture of two compounds of which the major component was 2,6-dideoxy-3,4-di-*O*-benzoyl-α-D-*ribo*-hexo-pyranosyl chloride.

Synthesis of Methyl 4-*O*-Benzoyl-2,6-dideoxy-3-*O*-(3,4-di-*O*-[*p*-methoxybenzoyl]-α-D-*ribo*-hexopyranosyl)-2,6-dideoxy-α-D-*lyxo*-hexopyranoside (14) and Methyl 4-*O*-Benzoyl-2,6-dideoxy-3-*O*-(3,4-di-*O*-[*p*-methoxybenzoyl]-β-D-*ribo*-hexopyranosyl)-2,6-dideoxy-α-D-*lyxo*-hexopyranoside (15).

From the Glycosyl Chloride 13. Compounds **14** [R_f 0.11, $[\alpha]_D$ +172° (c 0.15)] and **15** [R_f 0.13, $[\alpha]_D$ +172° (c 0.59)] were synthesized, each in 20% yield, from compounds **13** and **7** as described for the preparation of compounds **8** and **9**. NMR data for **14** and **15** are given in Tables 1 and 2. Anal. Calcd for $C_{36}H_{40}O_{12}$: C, 64.40; H, 6.18. Found: C, 64.78; H, 6.30 (Compound **14**) and C, 64.70; H, 6.34 (Compound **15**). 1,5-Anhydro-2,6-dideoxy-3,4-di-*O*-(*p*-methoxybenzoyl)-D-*ribo*-hex-1-enitol (**16**) (R_f 0.22, mp 67-69 °C, $[\alpha]_D$ +433° (c 0.088)) also was formed in this reaction in 49% yield. Anal. Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.45; H, 5.56.

From the Thioglycoside 2. Compounds **14** (42%) and **15** (40%) were synthesized from **2**[8] and **7** as described for the synthesis of **8** and **9** from the thioglycoside **17** and **7**.

ACKNOWLEDGMENTS

The authors wish to thank the Standard Oil Company for generous support of this research.

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