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Anomerization and transglycosylation reactions of permethylated methyl D-glycopyranosides

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ABSTRACT

The anomerization reactions of permethylated methyl D-glycopyranosides in the presence of various Lewis acid catalysts, such as Me_3SiOTf, Me_3SiOMs, $BF_3 \cdot OEt_2$, or $TiCl_4$ were examined in dichloromethane solution. β Anomers of the glycosides anomerized to the α anomer very rapidly, but the anomerizations in the opposite direction were slower. Transglycosylation reactions of the glycosides in the presence of similar catalysts and ethanol gave preferably the α anomers with most substrates employed. No anomerization was observed in the case of the α-mannoside, probably because the α anomer is strongly favored at equilibrium. Nevertheless, transglycosylation took place.

INTRODUCTION

The anomerization of glycosidic linkages has been a subject of much research[1]. The mechanism of the reaction is arguably diverse depending on substrates, catalysts, and reaction media. The investigation of the mechanism of this reaction has been done primarily with tetraacetates of pyranosides or pyranosides having free hydroxyl groups. In the course of our research on the reductive cleavage of glycosidic linkages, we came to examine the effect of various catalysts on the anomeric configuration of glycosides. As a part of the determination of the total structure of a polysaccharide, partial cleavage of the polysaccharide to disaccharides, trisaccharides, etc., is essential in determining the sequence and the anomeric configuration of the glycosidic linkages[2]. Therefore, information regarding the anomerization phenomena by the catalysts employed for the reductive-cleavage reaction should be available before any conclusion about the structure of the original polysaccharide is drawn from the physical properties of any oligosaccharide isolated from a polysaccharide. Herein we report our findings on the anomerization reactions of several permethylated methyl glycosides in the presence of

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TABLE I

Percent of anomerization of permethylated methyl D-glycopyranosides in the presence of various catalysts after 1 and 24 [a] h at 25°C

Catalyst (equiv)	α-Glc	β-Glc	α-Man	β-Man [b]	α-Gal	β-Gal
Me_3SiOTf (10)	11 (16)	81 (82)	0 (0)	90 (91)	15 (15)	85 [c] (85)
$BF_3 \cdot OEt_2$ (10)	5 (20)	3 (35)	0 (0)	57 (83)	15 (20)	80 (88)
5:1 Me_3SiOMs–$BF_3 \cdot OEt_2$	22 (22)	21 (21)	0 (0)	[d]	[d]	19 (20)
$EtSO_3H$ (5)	10 (15)	48 (85)	0 (0)	[d]	17 (17)	92 [c] (97)
$Me_3SiOCOCF_3$ (10)	0 (0)	0 (0)	0 (0)	[d]	0 (0)	0 (0)
Me_3SiOMs (10)	0 (0)	9 (0)	0 (0)	[d]	0 (0)	0 (0)
$TiCl_4$ (1)	0 (0)	100 (100)	0 (0)	100 (100)	[d]	100 (100)
$TiCl_4$ (0.1)	0 (0)	61 (70)	0 (0)	[d]	[d]	[d]

[a] Values in parentheses. [b] A mixture of α and β (82:18 mol ratio) anomers was used. [c] Similar conversion was achieved in 15 min. [d] Not examined.

various catalysts, including those generally employed in reductive-cleavage reactions.

RESULTS AND DISCUSSION

The catalysts which are widely used for the reductive cleavage of permethylated polysaccharides are trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) and boron trifluoride etherate ($BF_3 \cdot OEt_2$)[3]. Me_3SiOTf is known to cause total cleavage of glycosidic linkages, although it can cause isomerization of the pyranose to the furanose skeleton[4]. $BF_3 \cdot OEt_2$ is less reactive than Me_3SiOTf, and thus can produce disaccharides, etc., from permethylated polysaccharides[2]. On the other hand, a mixed catalyst comprised of a mixture of trimethylsilyl methanesulfonate (Me_3SiOMs) and boron trifluoride etherate (5:1 Me_3SiOMs–$BF_3 \cdot OEt_2$ mol ratio) results in total reductive cleavage without ring isomerization[5]. Therefore, Me_3SiOTf, Me_3SiOMs, Me_3SiOMs:$BF_3 \cdot OEt_2$, and $BF_3 \cdot OEt_2$ were included in this study.

Table I shows the extent of anomerization of several permethylated methyl D-glycopyranosides by several catalysts in dichloromethane solution. In the presence of Me_3SiOTf, β anomers of methyl D-glucoside and methyl D-galactoside formed equilibrium mixtures in which the α/β ratios were 4.26 and 5.66, respectively, within 1 h. Similarly, equilibrium was reached in 1 h with the α-galactoside. In contrast, the α anomer of the D-glucoside slowly changed to the β anomer and equilibrium was not yet reached after 24 h. At that time the α:β ratio was 5.25, and was still slowly changing. In the case of the α-D-mannoside no anomerization was observed with any catalyst employed because, in this case, the equilibrium mixture was nearly 100% α. When a mixture of the α- and β-D-mannopyranosides (α:β = 82:18 mol ratio) was used, ~ 90% of the β anomer changed into α in 1 h, and no further anomerization was apparent after 24 h.

$BF_3 \cdot OEt_2$ also resulted in slow anomerization, converting 35% of the β-glucoside into the α anomer after 24 h. The extents of anomerization were very significant with β-galactoside (88%) and β-mannoside (83%) after 24 h. The extent of the anomerization should be a concern when this catalyst is used for the partial reductive-cleavage reaction of a polysaccharide having β linkages. Neither Me_3SiOMs nor $Me_3SiOCOCF_3$ caused anomerization of any of the glycosides examined in the present investigation.

The mixed catalyst (5:1 Me_3SiOMs–$BF_3 \cdot OEt_2$ mol ratio) showed quite interesting activity. Both α- and β-glucosides reached an equilibrium in 1 h and the $\alpha:\beta$ ratio was ~ 4. A similar phenomenon was observed with the β-galactoside. The α-mannoside did not change at all because the α anomer predominates strongly in the equilibrium mixture. Me_3SiOMs was a component of the mixed catalyst for the reductive-cleavage reaction of glycoside linkages[5]. The fact that Me_3SiOMs did not cause anomerization is rather surprising in view of the mechanistic speculation on the reductive-cleavage and anomerization reactions. Gray et al.[6] suggested the formation of a cyclic oxonium-ion intermediate in the course of the reductive-cleavage reaction. A similar kind of the intermediate in the course of anomerization was postulated by Capon for the anomerization of methyl β-D-glucopyranoside[7]. It is not clear what role the catalyst plays in the formation of the cyclic oxonium-ion intermediate. However, one may speculate that the catalyst donates a cationic group (H^+ or Me_3Si^+) which accepts a lone pair of electrons from the oxygen atom in a glycosidic linkage, facilitating cleavage of the glycosidic bond and, eventually, leading to a cyclic oxonium-ion intermediate. The latter, once formed, will lead to the α anomer preferentially because of the so-called anomeric effect. The striking difference in catalytic activity of Me_3SiOTf and Me_3SiOMs strongly suggests that the actual group transfered in the reaction is the trimethylsilyl group. Indeed, the fact that $Me_3SiOCOCF_3$ and Me_3SiOMs do not cause anomerization may be explained by their inability to transfer the trimethylsilyl group. $BF_3 \cdot OEt_2$ in the mixed catalyst may make the trimethylsilyl group available by coordinating on one of the oxygen atoms of the sulfonyl group. The catalytic activities of Me_3SiOTf, $BF_3 \cdot OEt_2$, and $EtSO_3H$ (a protic acid) show a remarkable contrast: virtually similar activities with the α-glucoside and both galactosides but very different activities with the β-glucoside (Table I).

Titanium tetrachloride ($TiCl_4$) has been widely used for conversion of β anomers into α anomers[8,9]. However, conversion in the opposite direction has not been reported. Although the mechanism of anomerization by $TiCl_4$ was not investigated, the catalyst, when 1 equiv was used, was useful for the preparation of α anomers of various alkyl glucopyranoside tetraacetates from their β counterparts. One closely related examination was performed with per-*O*-benzylated glucopyranosides with $TiCl_4$ (ref. 10). We examined the effect of $TiCl_4$ on the permethylated methyl glycopyranosides in dichloromethane. When 1 equiv of $TiCl_4$ was present, β anomers of methyl glucoside, galactoside, and mannoside were converted quantitatively into their α forms within 15 min. On the other hand,

TABLE II

Composition (mol%) of the mixture of permethylated methyl D-glycopyranosides and Me_3SiOTf in the presence of ethanol (10 equiv) after 1 and 24 [a] h at 25°C

Substrate	α-OMe	β-OMe	α-OEt	β-OEt
α-Glc	37.3 (11.9)	1.5 (2.4)	45.1 (67.4)	16.1 (18.3)
β-Glc	11.8 (13.4)	2.5 (2.7)	66.8 (65.7)	18.9 (18.1)
α-Man	15.6 (9.9)	0.0 (0.0)	84.4 (90.1)	0.0 (0.0)
β-Man [b]	25.3 (8.1)	0.0 (0.0)	67.9 (86.2)	6.8 (5.7)
α-Gal	15.1 (15.7)	1.0 (2.0)	67.6 (72.8)	16.3 (9.5)
β-Gal	10.9 (11.4)	1.4 (1.7)	71.3 (71.8)	16.4 (15.1)

[a] Values in parentheses. [b] A mixture of α and β (82:18 mol ratio) anomers was used.

α anomers did not anomerize at all, even after 24 h. This indicates that the equilibrium mixture is nearly 100% α. When 0.1 equiv of $TiCl_4$ was employed, the rate of the anomerization of the β glucoside was significantly lower, resulting in 70% conversion after 24 h.

Next we examined the effect of the presence of ethanol (10 equiv) by measuring the extent of its incorporation into products (Tables II, III, and IV). Indeed, in the presence of Me_3SiOTf, ~85% of the methyl glucopyranosides were converted into ethyl glucopyranosides in which α was the favored configuration at the anomeric carbon atom (Table II). The equilibrium ratio of α-OEt to β-OEt was ~3.70 regardless of the starting glucopyranoside (α-OMe or β-OMe). β Anomers reached equilibrium faster than α anomers.

Permethylated methyl β-D-galactopyranoside showed a similar reaction, resulting in ~87% conversion into ethyl galactopyranosides. Under the same conditions, ~83% of the α-galactoside was converted into the ethyl compound. The ratios of α-OEt:β-OEt were 7.66 and 4.76 from the α- and β-galactopyranosides, respectively. These ratios are larger than from the glucose derivatives. The fact that the composition of the product mixtures is slightly dependent on the starting anomer shows that equilibrium is not complete. Nevertheless it seems clear that the α configuration is more favored with a galactoside than with a glucoside.

Transglycosylation was observed even with permethylated methyl α-D-mannopyranoside, leading to ~90% incorporation of ethanol. This result, together with the fact that no anomerization occurred during this reaction, is further demonstration that the α anomer is energetically more favorable, due to the trans disposition of the C-1–OCH_3 and C-2–OCH_3 groups, in the mannopyranoside skeleton.

Transglycosylation was much slower when $BF_3 \cdot OEt_2$ was employed (Table III) and it was the slowest in the presence of the mixed catalyst (Table IV). The latter observation seemed inconsistent with the rapid anomerization of the glycoside linkage. Although we do not have definite evidence, formation of the Me_3SiOMs–BF_3 complex under the protic conditions may be unfavorable compared to complexation with ethanol, which prevents the transglycosylation.

TABLE III

Composition (mol%) of the mixture of permethylated methyl D-glycopyranosides and $BF_3 \cdot OEt_2$ in the presence of ethanol (10 equiv) after 1 and 24 [a] h at 25°C

Substrate	α-OMe	β-OMe	α-OEt	β-OEt
α-Glc	98.0 (58.9)	0.0 (2.3)	0.8 (28.2)	1.2 (10.5)
β-Glc	0.5 (14.4)	94.0 (9.7)	1.8 (56.1)	3.6 (19.8)
α-Man	98.4 (53.3)	0.0 (0.0)	1.6 (46.7)	0.0 (0.0)
α-Gal	79.9 (11.5)	0.6 (0.9)	15.3 (70.3)	4.5 (17.3)
β-Gal	11.9 (12.5)	48.1 (1.5)	31.7 (73.3)	8.2 (13.1)

[a] Values in parentheses.

TABLE IV

Composition (mol%) of the mixture of permethylated methyl D-glucopyranosides and mixed catalyst (5:1 Me_3SiOMs–$BF_3 \cdot OEt_2$ mol ratio) in the presence of ethanol (10 equiv) at 25°C

Time (h)	α-Glc				β-Glc			
	α-OMe	β-OMe	α-OEt	β-OEt	α-OMe	β-OMe	α-OEt	β-OEt
1	100	0	0	0	0	100	0	0
4	100	0	0	0	0	98	0.7	1.2
20	100	0	0	0				
24	100	0	0	0	0	92.3	3.4	4.3
38	99.4	0	0.6	0				
48					0	85.5	6.0	8.3
62	99.1	0	0.9	0				
146					5.7	58.1	21.5	19.8
450	85.5	0	7.3	7.2				

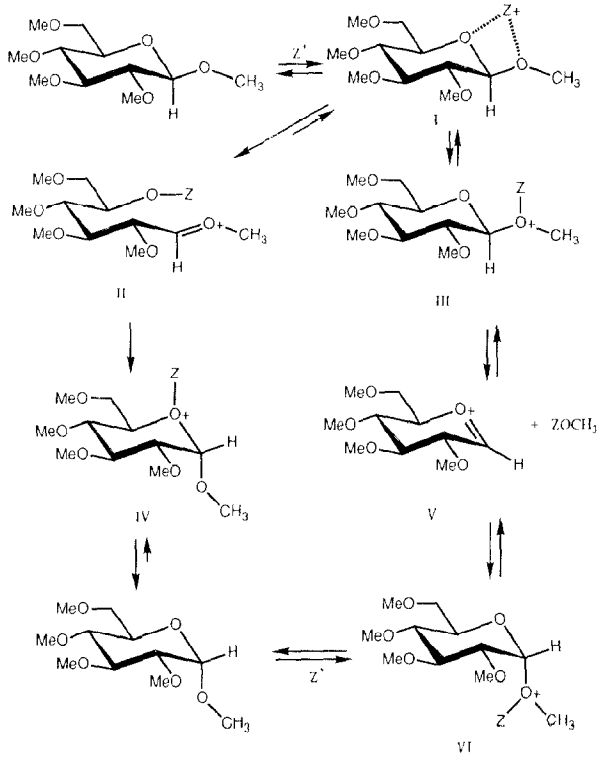
In order to examine the role of $TiCl_4$ in the anomerization reaction, we examined the effect of the presence of ethanol on the anomerization of permethylated methyl β-D-glucopyranoside (Table V). When the molar ratios of the substrates : $TiCl_4$: EtOH were 1 : 1 : 10, neither anomerization nor transglycosylation was observed. This result may be explained by the complete decomposition of $TiCl_4$ into $Ti(OEt)_4$, which is catalytically inactive. In fact, the order of mixing the reagents caused a significant difference. When $TiCl_4$ was added to a solution of

TABLE V

Mol% of the mixture from $TiCl_4$-catalyzed anomerization of methyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside in the presence of ethanol after 1 and 24 [a] h at 25°C

$TiCl_4$ (equiv)	EtOH (equiv)	α-OMe	β-OMe	α-OEt	β-OEt	OH
1	5	0.0 (0.0)	100 (74.2)	0.0 (13.0)	0.0 (12.8)	0.0 (0.0)
1	10	0.0 (0.0)	100 (100)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
5	1	16.4 (8.7)	15.5 (10.5)	0.0 (5.0)	0.0 (5.7)	68.1 (70.0)
10	10	0.0 (0.8)	2.5 (3.6)	16.5 (13.9)	24.9 (15.0)	56.0 (66.7)

[a] Values in parentheses.



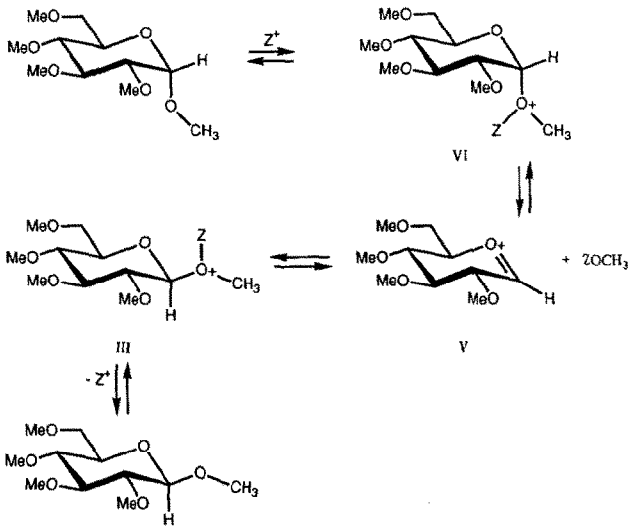
Scheme 1.

the substrate and ethanol (10 equiv) in dichloromethane, no change of the substrate was observed. On the other hand, when the ethanol was added to a solution of the substrate and $TiCl_4$ (1 equiv), 10–20% anomerization of the substrate took place (data not shown).

All experiments listed in Table V were performed by adding the catalyst last. The result with the ratio of 1:1:5 is understandable if we postulate a cyclic oxonium intermediate. As only ~ 26% of the substrate exchanged OMe for OEt, the ethanol was always in at least 19-fold excess and trapped almost all of the oxonium ion. Therefore, none of the α-OMe compound was formed.

When the amount of $TiCl_4$ was in excess, hydrolysis of the glycosidic bond took place during the work-up with sodium hydrogencarbonate solution, probably due to the HCl that was released.

The mechanism of anomerization of the permethylated methyl glycopyranosides appears to differ according to the anomeric configuration of the starting glycoside linkage. In the case of β anomers (Scheme 1) both the ring and glycosidic oxygen atoms can coordinate with the cationic catalysts simultaneously. Complexing with both oxygen atoms seems to be especially important in case of $TiCl_4$, as the β anomer is converted into the α anomer whereas conversion in the opposite



Scheme 2.

direction is not observed. Once the complex (**I**) is formed, it may undergo bond cleavage to give either a cyclic oxonium ion (**V**) or an acyclic oxonium ion (**II**). Although we do not have definite evidence of the formation of the latter intermediate, we speculate that the process of formation of **II** may be reversible and the equilibrium seems to be much more favorable in the direction of **II**. Once it is formed, the intermediate **II** may then undergo intramolecular recyclization to form **IV** irreversibly. Conversion of **IV** into the α anomer should be an extremely favorable process because of the unstable nature of positively charged oxygen in the pyranose ring. On the other hand, the intermediate **V** should undergo both anomerization and transglycosylation because both processes take place intermolecularly. As 10 equiv of ethanol was present, transglycosylation seemed to be the predominant reaction. We cannot rule out the route via β-**I** → **III** → **V** → **VI**-α as the sole pathway, and then the much more favorable formation of **I** as compared to **VI** may be attributed to much higher rates of anomerization and transglycosylation.

When the configuration of the starting glycoside is α, the formation of a complex in which two oxygen atoms are involved is unlikely (Scheme 2). Formation of only a cyclic oxonium intermediate (**V**) seems possible. Thus, the much lower rate of anomerization is understandable.

The order of the catalytic activities were $Me_3SiOTf > EtSO_3H > BF_3 \cdot OEt_2$. Apparently, the trimethylsilyl group donated from Me_3SiOTf can form a complex readily by using the *d* orbital of the silicon atom. On the other hand, the complex with boron trifluoride may be energetically unfavorable because of electronic repulsion between the lone-pair electrons of the F and O atoms. The much faster rate of anomerization of the β-D-galactopyranoside, and larger $\alpha:\beta$ ratio as

compared to the β-D-glucopyranoside, may be understood as a long-range field effect of the axial H_3CO-4 group, which may repel the lone-pair electrons in the glycosidic oxygen atom.

EXPERIMENTAL

Starting materials.—Methyl α- and β-D-glucopyranosides, methyl α-D-mannopyranoside, and methyl α- and β-D-galactopyranoside were all commercial products. Methyl β-D-mannopyranoside was not prepared as the pure isomer. Instead a mixture of α and β (82:18) anomers was prepared from D-mannose and MeOH by following a literature procedure[11]. Trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) and trimethylsilyl methanesulfonate (Me_3SiOMs) were prepared from trifluoromethanesulfonic acid and methanesulfonic acid, respectively, by refluxing with chlorotrimethylsilane. Boron trifluoride etherate, ethanesulfonic acid, and $TiCl_4$ were all commercial products. Dichloromethane was dried over CaH_2 and distilled prior to use.

Permethylated methyl D-glycopyranosides.—The procedures are essentially those of Fügedi *et al.*[12] and of Ciucanu *et al.*[13] To a solution of methyl D-glycopyranoside (7 mmol) in Me_2SO (28 mL) was added NaOH (84 mmol) and the mixture was stirred for 2 h. Methyl iodide (5.8 mL) was added and the flask was stoppered. After stirring for 5 h the solution was poured into ice–water (80 mL) and was extracted with $CHCl_3$ (3 × 35 mL). The organic layer was washed with water (2 × 35 mL) and dried (Na_2SO_4). The solvent was removed under vacuum at aspirator pressure and the residual gel-like product was distilled under vacuum; yield: α-D-Glc, 67%, bp 92°C (0.15 mm); β-D-Glc, 64%, bp 78–80°C (0.07 mm); α-D-Man, 67%, bp 92–93°C (2.00 mm), α-D-Gal, 60%, bp 90°C (0.1 mm); and β-D-Gal, 68%, bp 93°C (0.15 mm).

Analytical methods.—A Varian Vista-6000 gas chromatograph equipped with a capillary column (DB-1701, 30 m, 0.25 μm, 0.25 mm i.d.) was used for analysis of the monosaccharide derivatives. The running conditions were: initial temperature, 120°C; initial hold, 2 min; temperature, increase, 6°C/min; final temperature, 280°C; final hold, 10 min; injector temperature, 220°C; detector temperature, 250°C; carrier gas, He. Docosane was added as a standard and the concentration of each components was calibrated by the area ratios to the standard.

Anomerization reaction.—To a solution (2 mL) of a methyl glycoside (3.6×10^{-5} M) in CH_2Cl_2 was added a catalyst (10 equiv) and the reaction solution was divided into 6 to 12 V-vials (in the case of Me_3SiOTf the vials were silylated inside by treatment with 5% Me_2SiCl_2 in toluene), capped and stirred. The reaction was quenched by adding satd $NaHCO_3$ (0.5 mL) after a predetermined time interval. The organic layer was dried (Na_2SO_4) and examined by GLC. More than 95% of the α and β glycosides could be accounted for in most runs. The retention times of each glycoside were as follows (min): Me β-D-Glc, 9.01; Me α-D-Glc, 10.01; Et β-D-Glc, 9.70; Et α-D-Glc, 10.40; HO α-D-Glc, 12.10; Me α-D-Man, 10.06; Et

TABLE VI

Rates of anomerization of permethylated methyl α-D-glucopyranoside

Catalyst	k_1 (min^{-1})	k_2 (min^{-1})
Me_3SiOTf	$1.0(\pm 0.2)\times 10^{-2}$	$4.4(\pm 0.7)\times 10^{-2}$
$BF_3\cdot OEt_2$	$1.2(\pm 0.2)\times 10^{-4}$	$5.1(\pm 0.8)\times 10^{-4}$
$EtSO_3H$	$8.6(\pm 0.2)\times 10^{-4}$	$3.6(\pm 0.8)\times 10^{-3}$

α-D-Man, 10.90; Me β-D-Gal, 10.40; Me α-D-Gal, 10.51; Et β-D-Gal, 11.03; and Et α-D-Gal, 11.28.

Anomerization in the presence of EtOH.—To a solution (2 mL) of a methyl glycoside (3.6×10^{-5} M) in CH_2Cl_2 was added 10 equiv of abs EtOH (distilled over CaO and then over 4A molecular sieves), and then a catalyst (10 equiv). The solution was divided into 6 to 12 V-vials, capped, and stirred for a predetermined time interval after which the reaction was quenched by adding satd $NaHCO_3$ solution (0.5 mL). The organic layer was removed and the aqueous layer was extracted with CH_2Cl_2 (2×0.5 mL). The combined organic layer was examined by GLC and GLC–CI-mass spectrometry (Finnigan 4000-MST 95. We are indebted to the Mass Spectrometry Laboratory, University of Minnesota).

Rate studies of the anomerization reactions.—The rates of anomerization of permethylated methyl α-D-glucopyranoside were measured by the decrease in concentration of the substrate in the presence of Me_3SiOTf, $BF_3\cdot OEt_2$, or $EtSO_3H$. The first-order reversible reaction rate-constants k_1 and k_2 for the following reversible reaction were calculated from the slope of a plot of time vs. $\ln[(A_o - A_{oo})/(A_t - A_{oo})]$, which is k_{obs}, and then using the following equations[14]:

$$k_{obs} = k_1 + k_2$$

$$k_2 = [A]_{oo} k_{obs}/[A]_o$$

The results for the reaction are given in Table VI.

$$\text{Me } \alpha\text{-D-Glc} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{Me } \beta\text{-D-Glc}$$

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