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Reductive cleavage of glycosides with borane complexes in the presence of boron trifluoride etherate

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Abstract

Mixtures consisting of five equivalents each of borane · methyl sulfide and boron trifluoride etherate per equivalent of acetal or five equivalents of various amine–borane complexes and 10 equivalents of boron trifluoride etherate readily accomplished reductive cleavage of the glycosidic linkages of several per-*O*-methylated monosaccharides and polysaccharides. In all cases, the expected products were obtained in the expected molar proportions and no artifactual products were observed. Reductive-cleavage analysis using these reagents is particularly convenient because the reagents themselves are easy to handle and because subsequent acetylation of the products is accomplished in situ.

Keywords: Polysaccharide; Reductive cleavage; Boron–amine complexes; Borane·methyl sulfide; Boron trifluoride etherate

1. Introduction

Several shortcomings of standard methylation analysis prompted us to develop a new technique for the structural characterization of polymeric carbohydrates. This new technique is referred to as the "reductive-cleavage method" since its salient feature is the reductive cleavage of glycosidic carbon–oxygen bonds in fully methylated polysaccharides [1]. This method has already been shown to be applicable to the analysis of polysaccharides containing a wide variety of sugar residues [2–12] and covalently attached noncarbohydrate substituents [13–18]. Moreover, the method has also been

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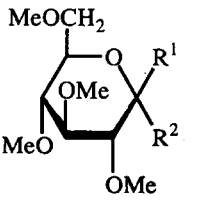
shown [19,20] to be applicable to sequence analysis through the proper choice of promoter for accomplishing selective reductive cleavage of susceptible glycosidic linkages.

Whether the method is used for the determination of ring form and position of linkage of monosaccharide residues or for the determination of their sequence, it is essential that the reductive cleavage reaction be carried out in high yield and that the ring form of the monosaccharide residue be preserved in the products. In the case of selective reductive cleavage, it is also essential that anomerization not take place at noncleaved glycosidic linkages. Toward this end, we have sought to identify reducing agents and catalysts that offer fidelity in the reductive-cleavage process. All of our past work has utilized triethylsilane as the reducing agent in the presence of either boron trifluoride etherate [1], trimethylsilyl trifluoromethanesulfonate [21], or a mixture [22] of trimethylsilyl methanesulfonate and boron trifluoride etherate as the promoter. Previous reports on the reductive cleavage of simple acetals by borane in tetrahydrofuran [23,24] and sodium borohydride in the presence of boron trifluoride etherate [23] suggested that boranes might be effective for the reductive cleavage of glycosides. Therefore, we examined borane complexes as reducing agents and the results are described herein.

2. Results

Methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranoside (**1**) and the corresponding β anomer **2** were used as model compounds for the determination of reaction rate and for optimizing reaction conditions. The reducing agent (borane complex) and promoter ($BF_3 \cdot Et_2O$) were added to the substrate in dichloromethane, and, at appropriate times, aliquots were withdrawn and the reaction was quenched by the addition of saturated aqueous sodium hydrogencarbonate. The organic layers were dried and analyzed by gas–liquid chromatography (GLC) and GLC combined with mass spectrometry (GLC–MS). Reactions showing complete disappearance of starting material were also analyzed by ^1H NMR spectroscopy in order to confirm the identity of products.



1 $R^1 = H, R^2 = OMe$
2 $R^1 = OMe, R^2 = H$
3 $R^1 = R^2 = H$

Table 1
Percentage of products derived by reductive cleavage of methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranoside (**1**) with $Me_2S \cdot BH_3$ in the presence or absence of $BF_3 \cdot Et_2O$

Reagents	Time (h)	Products (%)		
		1	**2**	**3**
$THF \cdot BH_3$ (5 equiv)	6	100		
	24	99		1
$Me_2S \cdot BH_3$ (5 equiv)	24	100		
	48	100		
$Me_2S \cdot BH_3$ (5 equiv) + $BF_3 \cdot Et_2O$ (1 equiv)	24	57	1	42
$Me_2S \cdot BH_3$ (5 equiv)	6	37	11	52
+ $BF_3 \cdot Et_2O$ (5 equiv)	18	5	2	93
	24			100

Borane · methyl sulfide complex and borane · tetrahydrofuran complex as the reducing agent.—Neither the borane · tetrahydrofuran complex ($THF \cdot BH_3$) nor the borane · methyl sulfide complex ($Me_2S \cdot BH_3$) reacted with **1** over a period of 24 h at room temperature (Table 1). Since $Me_2S \cdot BH_3$ is more stable and easier to handle than borane in tetrahydrofuran, further reactions were carried out with $Me_2S \cdot BH_3$ in the presence of $BF_3 \cdot Et_2O$ as the Lewis acid promoter. As is evident in Table 1, compound **1** was quantitatively converted to 1,5-anhydro-2,3,4,6-tetra-*O*-methyl-D-glucitol (**3**) when reductive cleavage was performed with 5 equiv each of $Me_2S \cdot BH_3$ and $BF_3 \cdot Et_2O$ for 24 h. If, however, only 1 equiv of $BF_3 \cdot Et_2O$ was used per equiv of glycoside, the rate of reductive cleavage of **1** was substantially slower (Table 1).

Amine–borane complexes as reducing agents.—Methyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside (**2**) was used as a model to examine the rate of reductive cleavage by various amine–borane complexes. Shown in Fig. 1 are the results obtained when the reductive cleavage of **2** was carried out at room temperature in the presence of trimethylamine · borane ($Me_3N \cdot BH_3$) and increasing amounts of $BF_3 \cdot Et_2O$. When reductive cleavage of **2** was carried out in the presence of 5 equiv each of $Me_3N \cdot BH_3$ and $BF_3 \cdot Et_2O$, the expected product **3** was produced in 82% yield after 24 h (Fig. 1A). The rate of reductive cleavage of **2** was substantially increased, however, when the ratio of $BF_3 \cdot Et_2O$ to $Me_3N \cdot BH_3$ was doubled (Fig. 1B). In this case, the expected product **3** was formed in quantitative yield after 24 h. A further increase in the ratio of $BF_3 \cdot Et_2O$: $Me_3N \cdot BH_3$ to 5:1, respectively, increased the rate of reductive cleavage of **2** only slightly (Fig. 1C). In all reactions, a small amount of anomerization of the β anomer **2** to the α anomer **1** was noted. It was concluded from these results that reductive cleavage was best carried out using 5 equiv of the amine–borane complex and 10 equiv of $BF_3 \cdot Et_2O$ per equiv of acetal.

The reductive cleavage of methyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside (**2**) was also carried out with four other commonly used amine–borane complexes under the same reaction conditions, i.e., 5 equiv of amine–borane and 10 equiv of $BF_3 \cdot Et_2O$ per equiv of acetal, and the results are presented in Fig. 2. All four reducing agents gave the expected product **3**, but at quite different rates. Reductive cleavages using morpholine · borane (Fig. 2A), 4-methylmorpholine · borane (Fig. 2B), and *tert*-butylamine · borane

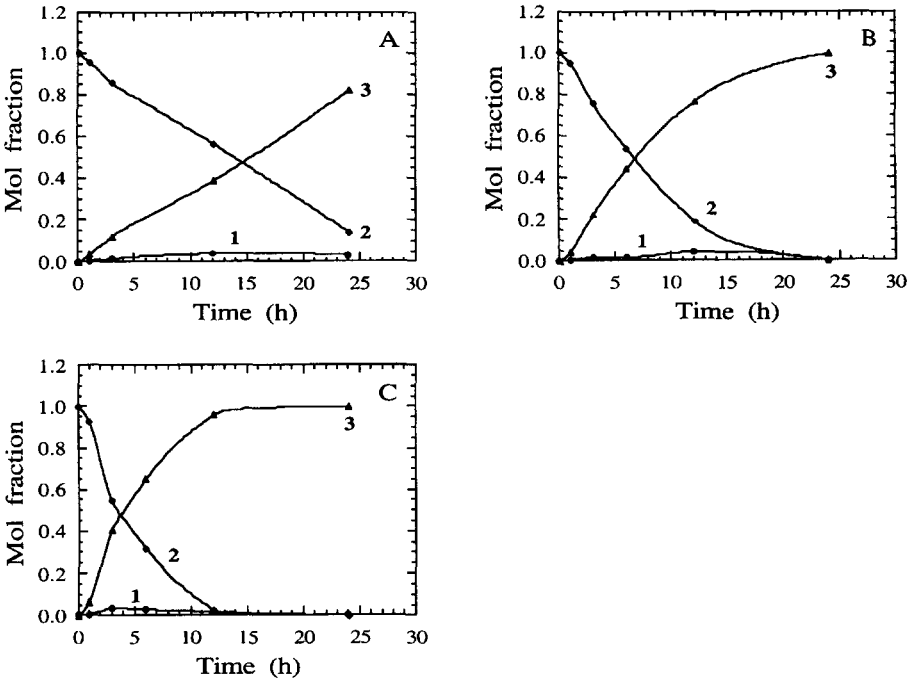
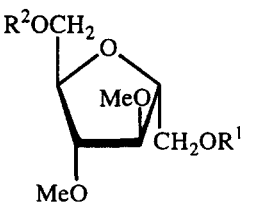


Fig. 1. Time-course of product formation during reductive cleavage of methyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside (**2**) in the presence of (A) $Me_3N \cdot BH_3$ (5 equiv) and $BF_3 \cdot Et_2O$ (5 equiv), (B) $Me_3N \cdot BH_3$ (5 equiv) and $BF_3 \cdot Et_2O$ (10 equiv), and (C) $Me_3N \cdot BH_3$ (5 equiv) and $BF_3 \cdot Et_2O$ (25 equiv).

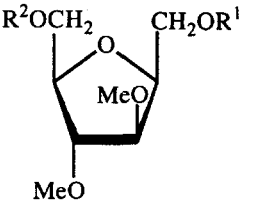
(Fig. 2C) all required more than 40 h for completion, whereas reductive cleavage using 2,6-lutidine · borane (Fig. 2D) was complete in 24 h. The rate of reductive cleavage by 2,6-lutidine · borane (Fig. 2D) was therefore quite comparable to that of trimethylamine · borane (Fig. 1B) when carried out under the same reaction conditions.

It was concluded from the combined results of these experiments that $Me_3N \cdot BH_3$ (5 equiv) in the presence of $BF_3 \cdot Et_2O$ (10 equiv) and 2,6-lutidine · borane (5 equiv) in the presence of $BF_3 \cdot Et_2O$ (10 equiv) were good candidates for performing reductive cleavage of fully methylated polysaccharides.

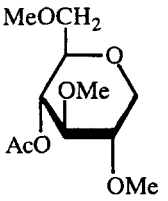
Reductive cleavage of per-O-methylated polysaccharides with borane complexes in the presence of boron trifluoride etherate.—Since $Me_2S \cdot BH_3$ in the presence of an equimolar amount of $BF_3 \cdot Et_2O$ and $Me_3N \cdot BH_3$ or 2,6-lutidine · BH_3 in the presence of a two-fold molar excess of $BF_3 \cdot Et_2O$ had accomplished complete reductive cleavage of the model compounds **1** and **2** in 24 h or less, these reducing systems were tested on fully methylated polysaccharides of known structure in order to evaluate their potential as reagents for structural analysis. Sucrose, cyclohexaamylose, pullulan, cellulose, inulin, and levan were selected for these experiments, and the products of reductive cleavage were acetylated in situ (see Experimental) and analyzed by GLC. Products were identified by comparison of their GLC retention indices and chemical-ionization (CIMS) and electron-ionization mass spectra (EIMS) to those of authentic standards [3,25]. The results are summarized in Table 2.



4 $R^1 = R^2 = Me$
6 $R^1 = Ac, R^2 = Me$
9 $R^1 = R^2 = Ac$



5 $R^1 = R^2 = Me$
7 $R^1 = Ac, R^2 = Me$
8 $R^1 = Me, R^2 = Ac$
10 $R^1 = R^2 = Ac$



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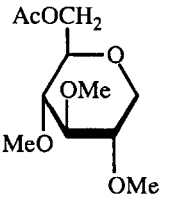

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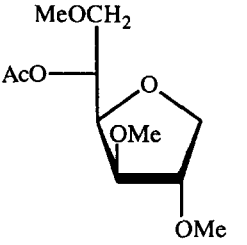

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Sucrose.—Reductive cleavage of per-*O*-methylated sucrose with $Me_2S \cdot BH_3$–$BF_3 \cdot Et_2O$ gave the expected products, namely 1,5-anhydro-2,3,4,6-tetra-*O*-methyl-D-glucitol (**3**), derived from the D-glucopyranosyl group, and both 2,5-anhydro-1,3,4,6-tetra-*O*-methyl-D-mannitol (**4**) and 2,5-anhydro-1,3,4,6-tetra-*O*-methyl-D-glucitol (**5**), derived from the D-fructofuranosyl group. The combined percentage of **4** + **5** (51.1%) was, within experimental error, equal to the percentage of **3** (48.9%). However, compounds **4** and **5** were formed in a substantially different ratio (~ 1:1) than in silane reductions wherein a ratio of 2.4:1, respectively, was observed when $BF_3 \cdot Et_2O$ was used as the promoter [3]. The order of addition of reducing agent and catalyst was found to be significant in this reaction. When $BF_3 \cdot Et_2O$ was added first to a solution of per-*O*-methylated sucrose in dichloromethane, the solution changed to dark brown instantly and, eventually, three unidentified peaks were observed as major products by GLC. However, when $Me_2S \cdot BH_3$ and $BF_3 \cdot Et_2O$ were added in that order, the expected products were obtained (Table 2). Therefore, all reductive-cleavage reactions were performed by sequentially adding the reducing agent and promoter to a solution of the fully methylated sugar in dichloromethane.

Inulin.—Inulin is a (2 → 1)-linked D-fructofuranose polymer terminated at its "reducing end" by a D-glucopyranosyl group. Reductive cleavage of the fully methylated polymer was therefore expected to give rise to 1,5-anhydro-2,3,4,6-tetra-*O*-methyl-D-glucitol (**3**), originating from the D-glucopyranosyl group, 2,5-anhydro-1,3,4,6-tetra-*O*-

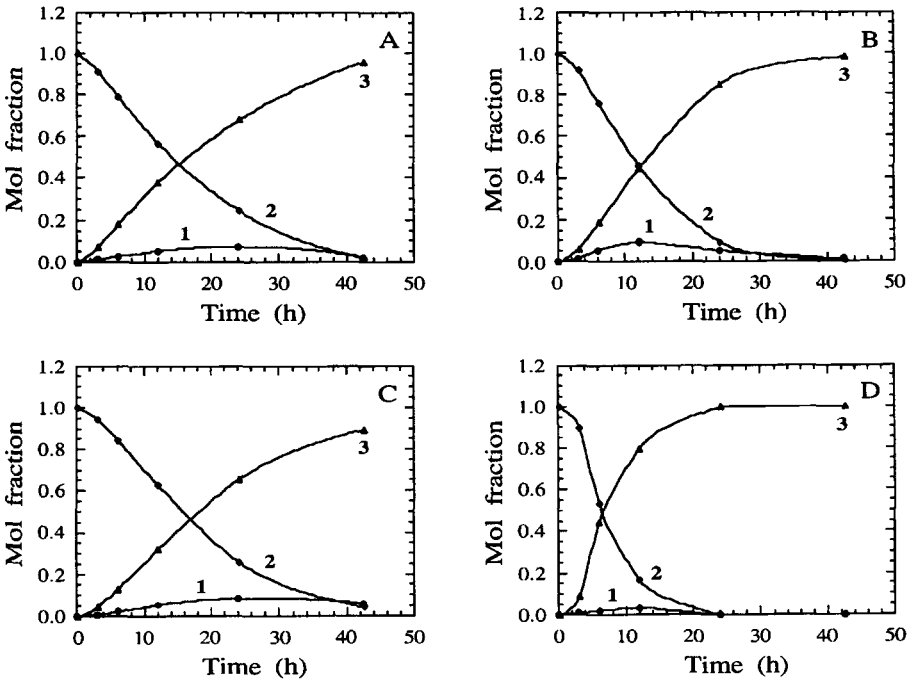

Fig. 2. Time-course of product formation during reductive cleavage of methyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside (**2**) in the presence of (A) morpholine·borane, (B) 4-methylmorpholine·borane, (C) *tert*-butylamine·borane, and (D) 2,6-lutidine·borane. All reactions were carried out in the presence of 5 equiv of reducing agent and 10 equiv of $BF_3 \cdot Et_2O$ per equiv of **2**.

methyl-D-mannitol (**4**) and 2,5-anhydro-1,3,4,6-tetra-*O*-methyl-D-glucitol (**5**), both originating from the nonreducing D-fructofuranosyl group, and 1-*O*-acetyl-2,5-anhydro-3,4,6-tri-*O*-methyl-D-mannitol (**6**) and 1-*O*-acetyl-2,5-anhydro-3,4,6-tri-*O*-methyl-D-glucitol (**7**), both originating from the (2 → 1)-linked D-fructofuranosyl residues. Indeed, with all the borane reducing agents employed (Table 2), the expected products were formed. The proportion of **3** was lower, however, than the combined proportions of **4** and **5**, indicating either that the D-glucopyranosyl group was absent in some of the polymer chains or that the product **3** derived from it was selectively lost during workup. The total proportion (91.8% av) of products **6** and **7** originating from the (2 → 1)-linked D-fructofuranosyl residues was that to be expected based upon previous work [3], but their relative proportions (~ 1:1.2) was noticeably different than in $BF_3 \cdot Et_2O$-promoted silane reductions wherein **6** and **7** were observed in a 2.7:1 ratio, respectively.

Levan.—Aerobacter levanicum levan is a D-fructan comprised of 6-linked and 1,6-linked D-fructofuranosyl residues and nonreducing terminal D-fructofuranosyl groups. Sequential methylation and reductive cleavage was therefore expected [3] to give 6-*O*-acetyl-2,5-anhydro-1,3,4-tri-*O*-methyl-D-mannitol (identical to **6**) and 6-*O*-acetyl-2,5-anhydro-1,3,4-tri-*O*-methyl-D-glucitol (**8**), originating from the 6-linked D-fructo-

Table 2
Percentage of products derived by reductive cleavage of per-*O*-methylated sucrose, inulin, levan, pullulan, cyclohexaamylose, and cellulose with borane complexes in the presence of $BF_3 \cdot Et_2O$

Polysaccharide	Reducing agent	Products (%)										
		3	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
Sucrose	$Me_2S \cdot BH_3$	48.9	24.9	26.2								
Inulin	$Me_2S \cdot BH_3$	2.7	3.2	3.8	43.0	47.3						
	$Me_3N \cdot BH_3$	3.0	2.7	2.7	42.3	49.3						
	2,6-lutidine $\cdot BH_3$	2.4	2.3	1.9	39.9	53.5						
Levan	$Me_2S \cdot BH_3$		3.8	4.2	31.5		52.5	3.7	4.3			
	$Me_3N \cdot BH_3$		5.5	5.2	23.3		59.0	2.2	4.8			
	2,6-lutidine $\cdot BH_3$		5.9	5.1	28.9		52.3	2.5	5.3			
Pullulan	$Me_2S \cdot BH_3$	3.3								64.5	32.2	tr
	$Me_3N \cdot BH_3$	3.5								64.3	32.2	
Cyclohexaamylose	$Me_2S \cdot BH_3$									100.0		
Cellulose	$Me_2S \cdot BH_3$	1.4								98.6		

furanose residues, 1,6-di-*O*-acetyl-2,5-anhydro-3,4-di-*O*-methyl-D-mannitol (**9**) and 1,6-di-*O*-acetyl-2,5-anhydro-3,4-di-*O*-methyl-D-glucitol (**10**), originating from the 1,6-linked D-fructofuranosyl residues, and compounds **4** and **5**, originating from the nonreducing terminal D-fructofuranosyl groups. Indeed, the expected products were formed with all the borane reducing agents employed (Table 2). Products **4** and **5** originating from the nonreducing terminal D-fructofuranose groups were formed in approximately a 1:1 ratio, as was also observed for sucrose and inulin. In contrast, reductive cleavage of 6-linked and 1,6-linked D-fructofuranosyl residues gave rise to products wherein those having the *gluco* configuration (**8** and **10**, respectively) predominated over those having the *manno* configuration (**6** and **9**, respectively). The latter results are the same as those obtained in silane reductions [3]. Quantitatively, these results are also in agreement with the results of silane reductions, i.e., the polysaccharide is comprised of approximately 82% 6-linked Fru*f* residues, 8% 1,6-linked Fru*f* residues, and 10% nonreducing terminal Fru*f* groups.

Pullulan.—The polysaccharide isolated from *Pullularia pullulans* is a linear D-glucan comprised of a trisaccharide repeating unit of one α-(1 → 6)-linked and two α-(1 → 4)-linked D-glucopyranosyl residues. Sequential methylation, reductive cleavage, and acetylation was therefore expected [4] to give 6-*O*-acetyl-1,5-anhydro-2,3,4-tri-*O*-methyl-D-glucitol (**12**) and 4-*O*-acetyl-1,5-anhydro-2,3,6-tri-*O*-methyl-D-glucitol (**11**) in the molar ratio of 1:2, respectively, as well as a small proportion of 1,5-anhydro-2,3,4,6-tetra-*O*-methyl-D-glucitol (**3**), originating from nonreducing terminal D-glucopyranosyl groups. Indeed, both $Me_2S \cdot BH_3$–$BF_3 \cdot Et_2O$ and $Me_3N \cdot BH_3$–$BF_3 \cdot Et_2O$ gave the expected products in the expected proportions. Only a trace of the ring isomerization product 5-*O*-acetyl-1,4-anhydro-2,3,6-tri-*O*-methyl-D-glucitol (**13**) was observed in the reductive cleavage using $Me_2S \cdot BH_3$–$BF_3 \cdot Et_2O$, and its proportion was too small to accurately integrate. The absence of **13** is significant as it is usually observed [4,26] as a product of reductive cleavage of 4-linked D-glucopyranosyl residues in reductive cleavages employing Et_3SiH and $Me_3SiOSO_2CF_3$. It should also be noted that the reductive cleavage of permethylated pullulan was complete under these conditions. This result stands in contrast to that obtained in $BF_3 \cdot Et_2O$-promoted silane reductions wherein the α-(1 → 6) glycosidic linkage is cleaved comparatively slowly.

Cyclohexaamylose.—This α-(1 → 4)-linked cyclic D-glucan was expected to give 4-*O*-acetyl-1,5-anhydro-2,3,6-tri-*O*-methyl-D-glucitol (**11**) as the only product after sequential methylation and reductive cleavage and, indeed, compound **11** was the only product that was observed when $Me_2S \cdot BH_3$ was tested as the reducing agent (Table 2).

Cellulose.—Reductive cleavage of per-*O*-methylated cellulose with $Me_2S \cdot BH_3$–$BF_3 \cdot Et_2O$ and subsequent acetylation of the product gave 1.4% of 1,5-anhydro-2,3,4,6-tetra-*O*-methyl-D-glucitol (**3**), derived from the nonreducing terminal D-glucopyranosyl group, and 98.6% of 4-*O*-acetyl-1,5-anhydro-2,3,6-tri-*O*-methyl-D-glucitol (**11**), derived from the internal β-(1 → 4)-linked D-glucopyranosyl residues (Table 2). It should be noted that this result stands in marked contrast to the result [4] of $BF_3 \cdot Et_2O$-promoted silane reductions wherein no reductive cleavage was observed. Compound **13**, arising from 4-linked D-glucopyranosyl residues via ring isomerization, was not detected when the reductive cleavage of permethylated cellulose was carried out with $Me_2S \cdot BH_3$–$BF_3 \cdot Et_2O$ (Table 2).

3. Discussion

Borane · methyl sulfide and various amine–borane complexes in the presence of boron trifluoride etherate are very effective reagents for the reductive cleavage of permethylated carbohydrates. The ease with which the reagents can be handled and the simple workup procedure offer advantages over previously reported reductive cleavage conditions. Additionally, the ability to carry out in situ acetylation in the presence of borate is particularly advantageous since no evaporation or further processing of the sample is required. The combination of $Me_2S \cdot BH_3$ and boron trifluoride etherate has already been demonstrated to be superior to other reductive cleavage reagents for the analysis of sialic acid-containing carbohydrates [9], and studies are in progress to determine whether these findings are generalizable to sugars of other classes.

4. Experimental

General.—Methylation was accomplished as described by Ciucanu and Kerek [27] and the fully methylated polysaccharides were purified by chromatography on Sephadex LH-20 [28]. Borane · methyl sulfide (1.0 M in CH_2Cl_2), borane · tetrahydrofuran (1.0 M in THF), and all amine–borane complexes were obtained from Aldrich Chemical Co. and used without further purification. Analytical GLC was performed on a Hewlett–Packard 5890 gas–liquid chromatograph equipped with a Hewlett–Packard 3392A integrator, a flame-ionization detector, and a Hewlett–Packard fused-silica capillary column (0.2 mm × 25 m) of cross-linked methylsilicone (0.33 μm film thickness). The temperature of the column was held at 110°C for 2 min, then programmed to 300°C at 6°C/min. GLC–MS analyses were performed using a Finnegan 4000 mass spectrometer equipped with a VG Multispec data system. Column effluents were analyzed by chemical-ionization mass spectrometry with NH_3 as the reagent gas and by electron-ionization mass spectrometry in order to verify that eluted components had mass spectra identical to those of authentic standards.

Time-course studies.—The rates of reductive cleavage of methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranoside (**1**) and the corresponding β anomer **2** were determined using different molar ratios of reducing agent and promoter. The following procedure is representative. An aliquot (0.25 mL) of **1** (0.063 mmol; 0.25 M in CH_2Cl_2) and 1.0 mL of CH_2Cl_2 (predried over CaH_2) were placed in a 10-mL vial and 0.31 mL (0.31 mmol) of M $Me_2S \cdot BH_3$ in CH_2Cl_2 and 38 μL (0.31 mmol) of $BF_3 \cdot Et_2O$ were sequentially added. The vial was capped, and at appropriate intervals aliquots were withdrawn and quenched with water then extracted with 3 × 10 mL portions of CH_2Cl_2. The CH_2Cl_2 extracts were dried over anhyd K_2CO_3, then concentrated and analyzed by GLC. Samples showing complete reductive cleavage were analyzed by GLC–CIMS and –EIMS and ^1H NMR spectroscopy in order to verify that **3** was the sole product.

Reductive cleavage and in situ acetylation.—The procedure for per-*O*-methylated inulin is representative. Into a 10-mL pear-shaped flask provided with a rubber septum and a magnetic stirring bar were added 0.11 mL (0.05 mmol of acetal; 0.45 M in CH_2Cl_2) of per-*O*-methylated inulin and 10 mL of freshly distilled CH_2Cl_2. Borane ·

methyl sulfide (0.25 mL; M in CH_2Cl_2) and $BF_3 \cdot Et_2O$ (30 μL) were then added with stirring, and the reaction mixture was stirred for 24 h at room temperature. The reaction was then quenched by the addition of 0.1 mL of water, and, after stirring for 30 min, 2 mL of Ac_2O and 0.2 mL of 1-methylimidazole were added. After stirring for an additional 30 min, 5 mL of water was added to destroy excess acetic anhydride, and the mixture was extracted with 4×5 mL portions of CH_2Cl_2. The organic extract was then extracted with 2×5 mL portions of water, dried (anhyd K_2CO_3), and evaporated under a stream of nitrogen.

Acknowledgement

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