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COMMUNICATION

Harnessing the Reactivity of Poly(methylhydrosiloxane) for the Reduction and Cyclization of Biomass to High-Value Products

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Poly(methylhydrosiloxane) (PMHS) has been examined for its ability to reduce and subsequently cyclize carbohydrate substrates using catalytic tris(pentafluorophenyl)borane (BCF). The work herein is the first reported example of the direct conversion of monosaccharides to 1,4-anhydro and 2,5-anhydro products utilizing a hydrosiloxane reducing agent. PMHS is produced from waste products of the silicone industry, making it a green alternative to traditional hydrosilane reducing agents. This work thus contributes to the goal of utilizing renewable feedstocks in the production of fine-chemicals.

Introduction

Alternative methods to produce liquid fuels and chemical commodities are needed to decrease dependence on fossil resources. The highly functionalized and stereochemically rich nature of cellulosic biomass makes it especially attractive in the production of fine chemicals, as a high degree of functionality can be translated to products that are desirable as synthons to a variety of industries.¹⁻⁴ However, the over oxygenated nature of biomass requires selective deoxygenation protocols to arrive at useful synthons. The metal-free deoxygenation of carbohydrates has been studied extensively by our group through the combination of catalytic tris(pentafluorophenyl)borane (BCF) and hydrosilane reducing agents. Site selectivity in C–O bond reduction for specific carbohydrates can be achieved by exploiting subtle steric effects and, in some instances,

neighboring group participation. For example, treatment of per-Et₃Si protected glucose with EtMe₂SiH under BCF catalysis results in rapid ring opening via reduction at the anomeric carbon (C1), followed by the slow but selective deoxygenation at the sterically most accessible primary carbon centers, affording 1,6-deoxysorbitol as the major product (Scheme 1a).⁵ Further studies demonstrated that a variety of silyl-protected sugar alcohols afford 1,6-deoxy products when treated with excess EtMe₂SiH and catalytic BCF, with further reduced species being minor by-products.⁶ Interestingly, galactitol yielded a 1,2,6-deoxy triol as the major product. Mechanistic studies elucidated the formation of a transiently formed tetraol that quickly cyclizes from O2 to C5 (with inversion at C5) before experiencing selective reduction at C2 (Scheme 1b). Later work demonstrated the ability of catalytic quantities of silylium to cyclize a variety of sugar alcohols to high-value 1,4-anhydro products in good to excellent yields (Scheme 1c).⁷ Effective catalysis was achieved by generating silylium in situ through hydride abstraction from EtMe₂SiH with trityl cation. The use of BCF as a Lewis acid led to poor conversions and to the occasional formation of 1,4-anhydro products, such as in the cyclization of sorbitol to 1,4-anhydrosorbitol. In situ monitoring by ¹⁹F{¹H} NMR spectroscopy traced the poor performance of BCF to its preferential coordination to the cyclic ether of the 1,4-anhydro product, which inhibits its ability to activate silane.⁸ Besides the reaction shown in Scheme 1a, few hydrosilylative reductions starting from cyclic sugars have been documented. One reported case uses in situ generated (C₆F₅)₂BH as a catalyst for the reductive ring-opening of per-silylated sugars to linear sugar alcohols with tetramethylhydrosiloxane (TMDS) as the reductant (Scheme 1d).⁹ However, reaction rates were sluggish for fully oxygenated sugars (e.g. TMS-protected D-glucose converted to TMS-sorbitol in only 14% yield after 14 days).

A drawback to the reduction chemistry described above is its reliance on hydrosilanes, which suffer from poor atom-economy. While hydrosilanes feature favorable thermodynamic and kinetic properties for C–O bond reduction, the stable Si–O bonds in the resulting silanol and siloxane by-products are energy intensive to

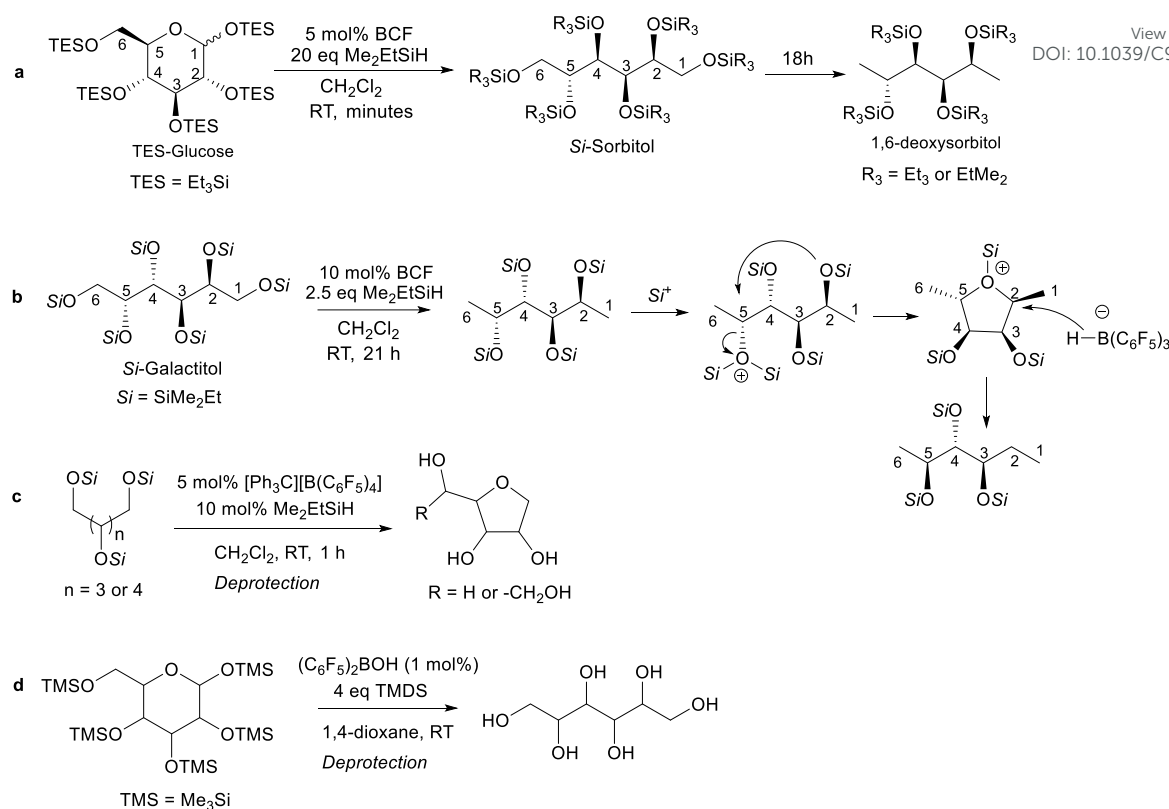
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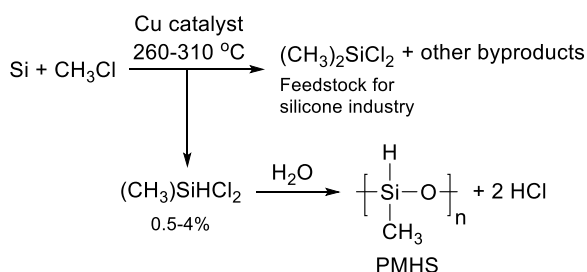
All ¹H and ¹³C NMR spectra (and data files) reported herein are also available at the spectroscopic database that we have established.
<http://gagnegroup.web.unc.edu/sugars-spectroscopy/sugars>.



Scheme 1. **a**) TES-protected glucose experiences ring-opening and selective reduction at the primary carbon centers when treated with EtMe_2SiH . **b**) Galactitol selectively forms a triol via cyclization/reduction of a transiently formed tetraol. **c**) Sugar alcohols cyclize to 1,4-anhydro products in good yields via catalytic silylium (R_3Si^+). **d**) Cyclic sugars reduce to sugar alcohols in the presence of TMDS and in situ generated $(\text{C}_6\text{F}_5)_2\text{BH}$.

recycle.¹⁰ An alternative, greener strategy is to instead exploit the reactivity of hydrosiloxanes, such as poly(methylhydrosiloxane) (PMHS), which are derived from waste products. PMHS is synthesized by the controlled hydrolysis of MeSiHCl_2 ,¹¹⁻¹² which is a by-product in the production of Me_2SiCl_2 , a feedstock for the silicone industry (Scheme 2).¹³ In addition to being synthesized from a waste product, PMHS is cheap, stable to air and moisture, and is considered nontoxic.¹² Numerous examples of reduction processes that utilize PMHS exists in the literature,^{12, 14-20} but an investigation into its use in the reduction of biomass is relatively unexplored.²¹⁻²⁶

The work herein explores the reactivity of PMHS with catalytic BCF in the reduction and subsequent cyclization of



Scheme 2. The Müller-Rochow process for the synthesis of $(\text{CH}_3)_2\text{SiCl}_2$, the main feedstock for the silicone industry. $(\text{CH}_3)_2\text{SiHCl}_2$ is a by-product from this process and can be used to synthesize PMHS.

carbohydrates. Careful control of the PMHS stoichiometry allows for the selective isolation of linear sugar alcohols or cyclized products derived therefrom. Cyclization processes differ across the investigated sugars, indicating that the subtle interactions between the substrate and the PMHS chain are affected by the sugar stereochemistry.

Results and Discussion

Initial studies probed the differences in reactivity between PMHS chains of variable length. Commercially available TMS-capped PMHS with M_n of 390, corresponding to an average of 4 Si-H units per chain, was compared to PMHS with M_n 1,700-3,200 (26-51 monomers) in the reduction and cyclization of TMS-protected D-glucose. These two different PMHS chain lengths are denoted as oligomeric and polymeric, respectively. Reaction progress was monitored in situ by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and a comparison of the extent of reactivity based on the equivalents of PMHS monomer per glucose is shown in Figure 1. Under catalytic conditions with 10 mol% BCF and using DCM as the solvent, both forms of PMHS reduce TMS-D-glucose to TMS-sorbitol **1** (in under 1 hour), followed by the slower cyclization to 1,4-anhydrosorbitol **2** (Scheme 3). However, oligomeric PMHS requires higher equivalents of monomer per glucose to reach product conversions comparable

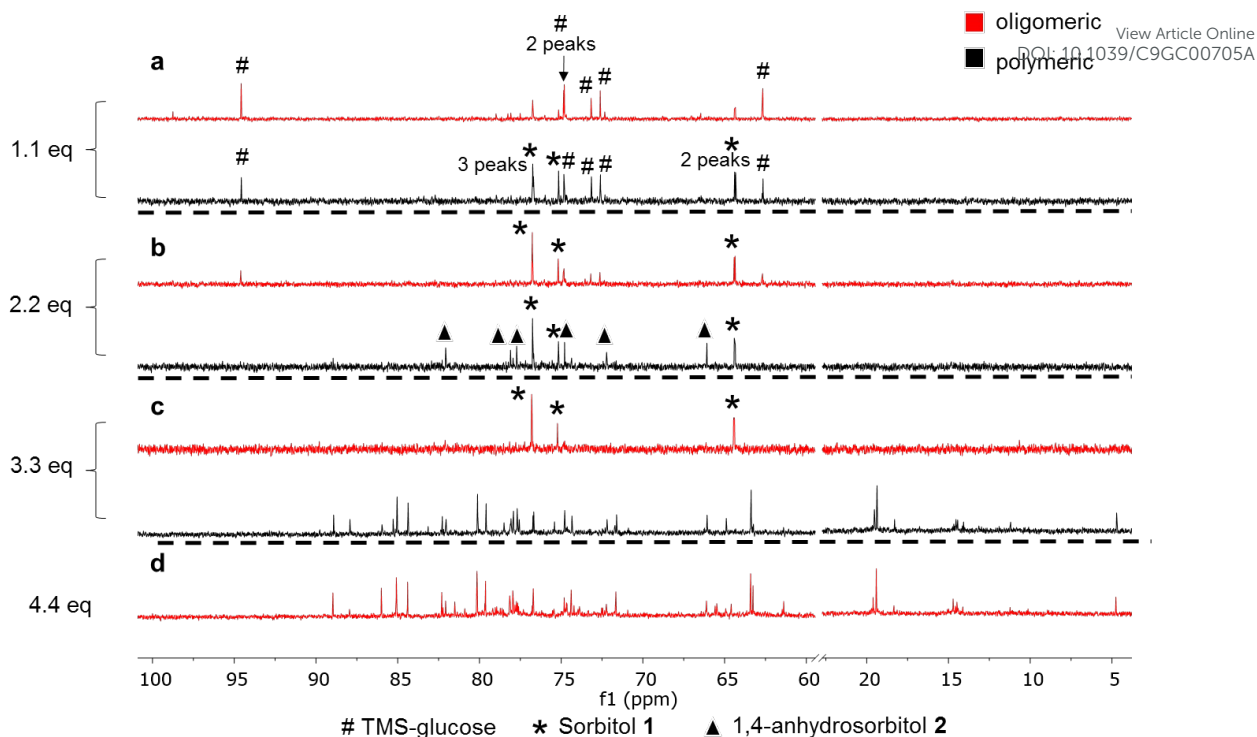
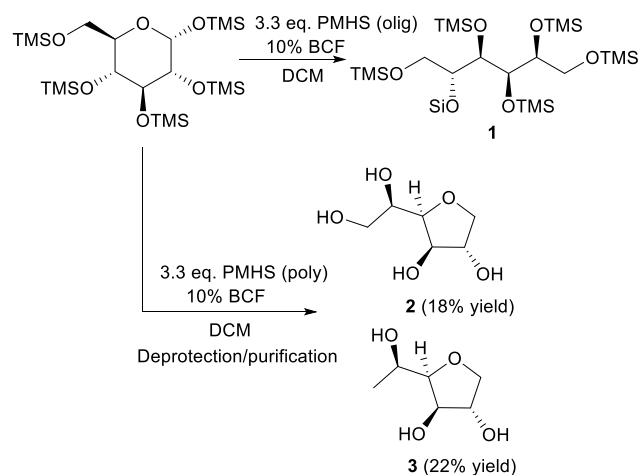


Figure 1. A comparison of in situ $^{13}\text{C}\{^1\text{H}\}$ NMR spectra monitoring the extent of reaction between oligomeric and polymeric PMHS towards TMS-D-glucose. Catalysis was performed using 10 mol% BCF with DCM as the solvent and all reactions were assayed after 24 h. **a)** 1.1 equivalents of oligomeric PMHS results in unreacted TMS-glucose with minor conversion to **1**, while polymeric PMHS affords roughly 50% conversion to **1**. **b)** 2.2 equivalents of oligomeric PMHS results in nearly full conversion to **1** with trace amounts of glucose remaining. 2.2 equivalents of polymeric PMHS results in a mixture of **1** and the cyclized species **2**. **c)** Full conversion to **1** is achieved with 3.3 equivalents of oligomeric PMHS but further reduction of **2** occurs with 3.3 equivalents of polymeric PMHS. **d)** 4.4 equivalents of oligomeric PMHS results in a complex product mixture from the reduction of **2**.

to those obtained with polymeric PMHS. For example, 3.3 equivalents of oligomeric PMHS are required to fully convert TMS-glucose to sorbitol, compared to nearly complete conversion when 2.2 equivalents of polymeric PMHS are used. Since the number of Si-H equivalents needed in the oligomeric PMHS roughly coincides with the size of an average chain, it suggests that once the first Si-H has reacted, a second one is not accessible in these short chains. The lower equivalents needed to reach similar conversions with polymeric PMHS implies that a more efficient use of Si-H groups is possible. When 3.3 equivalents of polymeric PMHS or 4.4 equivalents of oligomeric PMHS are used, further deoxygenation of **2** is apparent by the increase in the number of upfield carbon signals. Following deprotection and purification by column chromatography, 6-deoxy-1,4-anhydrosorbitol **3** was isolated from this mixture, along with recovered **2**. Due to the enhanced reactivity of polymeric PMHS, along with its lower cost, the optimization of reaction conditions was pursued with this material.

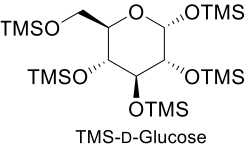
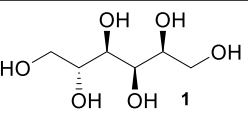
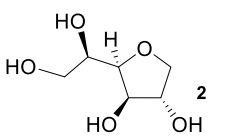
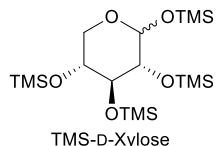
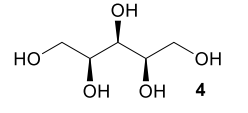
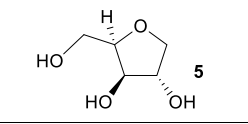
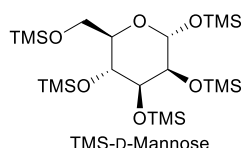
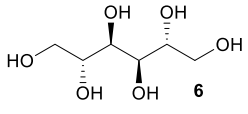
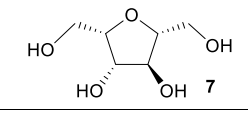
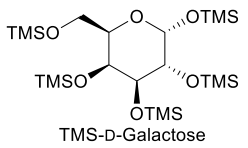
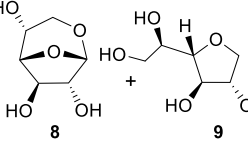
A select number of TMS-protected sugars were investigated for their reactivity with polymeric PMHS under BCF catalysis. Reactions were performed in DCM with 10 mol% loading of BCF and reaction progress was monitored in situ by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. Samples were then deprotected using Dowex® resin in methanol, followed by hydrolysis of the PMHS byproduct by heating in water to 50 °C to separate the sugar products from the siloxane. These conditions were found to be

the least involved and costly to obtain polyol products free of Si-byproducts, and in reasonable yields. Table 1 displays the number of equivalents of polymeric PMHS required to yield linear sugar alcohols or to convert to cyclized product. The initial



Scheme 3. When reduction of glucose is performed with 3.3 equivalents of oligomeric PMHS, full conversion to **1** is achieved. Treatment of glucose with 3.3 equivalents of polymeric PMHS results in a complex product mixture, from which **2** and **3** can be isolated following deprotection.

Table 1. Products resulting from the reduction and cyclization of monosaccharides under BCF catalysis with PMHS. Workup to remove siloxane byproducts is column free

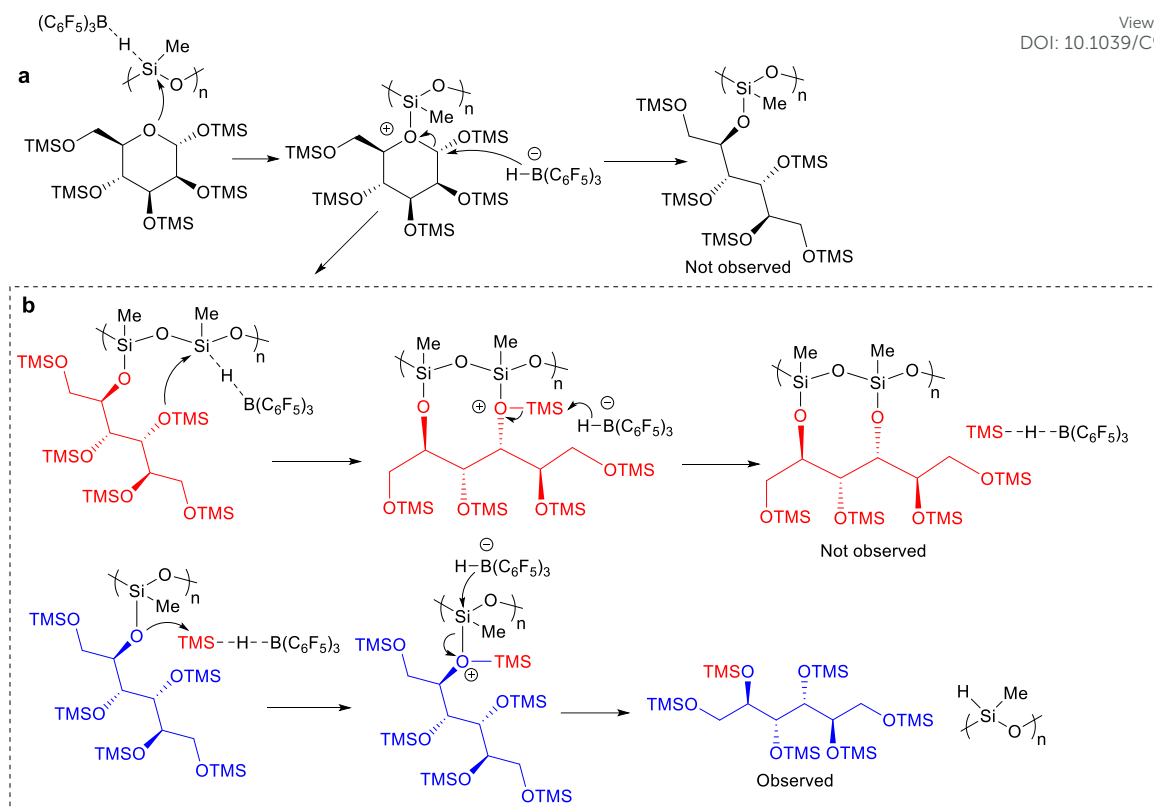
Substrate	Equivalents PMHS	Products	Purity/Yield (%)
 TMS-D-Glucose	1.8	 1	89/68 ^a
	2.3	 2	81/58 ^b
 TMS-D-Xylose	1.3	 4	76/48 ^a
	1.5	 5	79/49 ^b
 TMS-D-Mannose	1.5	 6	87/54 ^a
	2.0	 7	85/67 ^c
 TMS-D-Galactose	2.0	 8 + 9	76/58 ^d

Reaction conditions: Premix substrate with 10 mol% BCF in CD₂Cl₂ (0.6 mL), followed by addition of PMHS. ^aReaction complete after 1 hour. ^bReaction complete after 24 hours. ^cReaction complete after 36 hours. ^dReaction complete after 24 hours, combined yield of **8** and **9** (~1:1), for cleanest reactivity PMHS and BCF were premixed before addition to the TMS-galactose.

reduction of the protected sugar to the linear sugar alcohol is rapid (complete in under 30 minutes), but the subsequent cyclization requires at least 24 hours to reach completion. Reactivity can be halted at the sugar alcohol and further conversion to cyclized product does not occur unless the specified equivalents of PMHS are added. For example, when monitoring the reduction of TMS-D-glucose to sorbitol with 1.8 equivalents of PMHS by in situ ¹³C{¹H} NMR spectroscopy, reactivity stops at the initial reduction to TMS-sorbitol and cyclization does not occur even after 3 days. To ascertain how PMHS reductions perform across a swath of biomass-derived starting materials, yields of product obtained using the column

free method of siloxane removal described above, along with percent purity, are reported in Table 1 for the optimized protocol. The ESI contains the ¹H and ¹³C{¹H} NMR spectra for the crude products after siloxane hydrolysis. Each product has been previously reported and can be purified in accordance with established protocols.^{7, 9, 27} While TMS-D-glucose and TMS-D-xylose both afford 1,4-anhydro products, TMS-D-mannose instead yields the 2,5-anhydro isomer **7**. TMS-D-galactose cannot be reduced to the sugar alcohol galactitol under the conditions studied, and instead always yields a mixture of 1,6-anhydrogalactofuranose **8** and 1,4-anhydrogalactitol **9**, even when 1.1 equivalents of PMHS are used in the reaction (see ESI). The order of addition for reagents was varied in the case of TMS-galactose reactivity; premixing PMHS and BCF minimizes the over reduction of **9** observed when TMS-D-galactose was added before the PMHS.

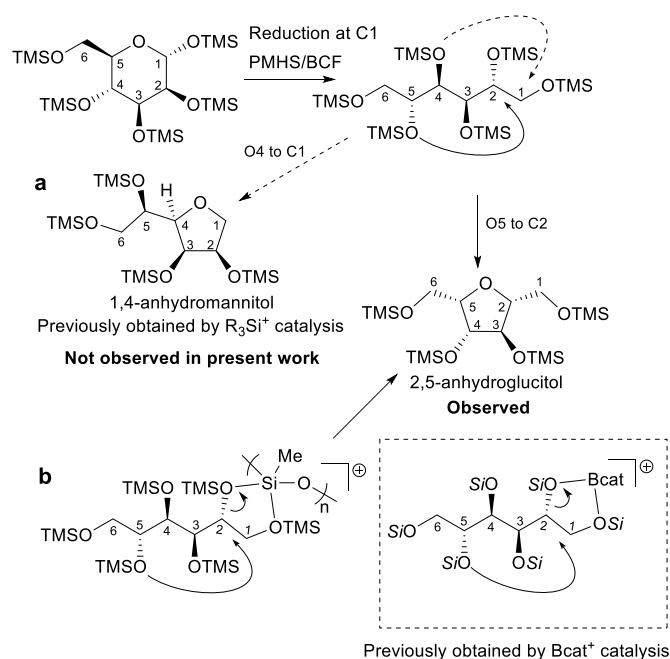
An important mechanistic consideration when comparing the differences in reactivity shown in Table 1 is whether the sugar is tethered to the PMHS chain following the initial reduction. Evidence from the reduction of TMS-D-mannose to mannitol indicates that the mannitol product is not protected by the PMHS chain, as would be expected in a simple mechanism (Scheme 4a). Instead, a symmetric ¹³C{¹H} NMR spectrum consisting of three oxygenated carbon signals and three TMS carbon signals is observed in situ. A PMHS protecting group would break symmetry and six unique oxygenated carbon signals would result (Scheme 4a). Formation of per-TMS-mannitol in the reaction was confirmed by spiking the reaction mixture with authentic compound. This provided a sample with complete overlap of resonances in the ¹³C{¹H} NMR spectrum. Since BCF is known to catalyze silyl group exchange between hydrosilanes and silyl ethers/siloxanes²⁸⁻²⁹, we hypothesized that silyl exchange might be facile, and that the resulting PMHS-protected sugar might not be visible due to its now polymeric nature. Depending on the extent of the exchange, this process could liberate half an equivalent (or more) of per-TMS-mannitol (Scheme 4b). Integration of the ¹H NMR signals for TMS-mannitol from in situ reduction of per-TMS-mannose relative to a cyclooctane internal standard gave a yield of 55%, providing support for this hypothesis. To demonstrate silyl exchange between two different silyl protected sugars in the presence of BCF and PMHS, an NMR scale reaction containing in situ produced TMS-mannitol (from TMS-mannose reduction with 10% BCF and 1.5 equiv. PMHS) was spiked with per-EtMe₂Si-mannitol. The resulting ¹³C{¹H} NMR spectrum contained broadened signals in the C–O region due to the complex mixture of silyl protected products obtained from exchange between TMS and EtMe₂Si groups. A similarly broadened ¹³C{¹H} NMR spectrum resulted from treating equimolar amounts of premixed TMS-mannose and EtMe₂Si-mannose with 1.5 equivalents of PMHS under BCF catalysis (see ESI). The control experiment where equimolar amounts of TMS-mannitol and EtMe₂Si-mannitol standard are treated with 10% BCF in the absence of PMHS predominantly yields sharp, discernable peaks for the two protected forms in the ¹³C{¹H} NMR spectrum. Together these results indicate that silyl exchange under catalytic conditions is facile and, moreover, that the hydrides of PMHS are needed to facilitate silyl exchange.



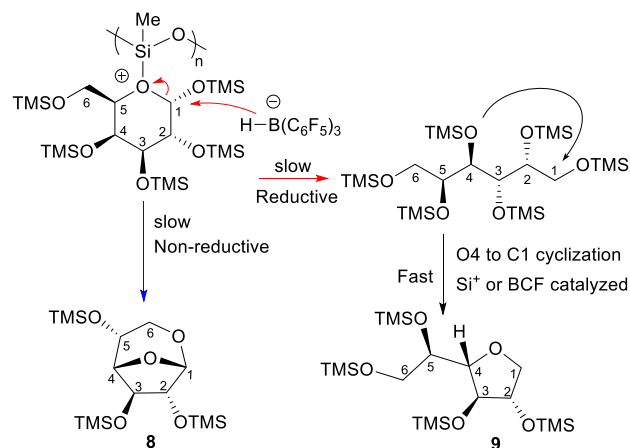
Scheme 4. a) The activation and subsequent reduction of TMS-D-mannose by PMHS and BCF would yield TMS-mannitol tethered to the PMHS chain (not observed). b) To support the observation of per-TMS-mannitol in situ, silyl group metathesis is invoked between PMHS and TMS, with transiently produced trimethylsilane driving the process.

The above analysis suggests that the cyclization of sugar alcohols occurs in an intermolecular fashion with PMHS derived silylium rather than intramolecularly from a tethered siloxane such as that shown in Scheme 4a. The O4 to C1 cyclization process yielding **2** and **5** has been previously demonstrated by the silylium catalyzed cyclization of silyl-protected sorbitol.⁷ However, the rationale for the O5 to C2 cyclization of **6** to **7** is less clear. Previous work established that under silylium catalyzed conditions, protected mannitol cyclizes O4 to C1, yielding 1,4-anhydromannitol (Scheme 5a).⁷ The conversion of mannitol to **7** via O5 to C2 cyclization has been previously reported under debenzylative cyclization conditions³⁰ or via boronium chelated precyclization intermediates.²⁷ The latter example of 1,2-boronum chelation driving the activation of the secondary position in sugar alcohols (boxed intermediate in Scheme 5b) suggests that PMHS derived silylium may be prone to accessing hypervalent silicon²¹ that similarly chelates the substrate and alters the stereoselectivity of the cyclization (Scheme 5b). Since hypervalency of PMHS silicon has been used to explain the means by which catalytic poly(ethylene glycol) crosslinks PMHS chains by homodehydrocondensation, this hypothesis is not entirely without merit.³¹

The product distribution resulting from TMS-D-galactose reduction is more puzzling. When the reaction mixture resulting from treatment of TMS-D-galactose with 2 equivalents of PMHS monomer is monitored in situ by ¹³C{¹H} NMR spectroscopy, one observes unreacted starting material and 1,4-



Scheme 5. a) Previous work has demonstrated that TMS-mannitol cyclizes O4 to C1 with catalytic silylium ($EtMe_2Si^+$). b) The formation of a transient 1,2-chelate between mannitol and hypervalent silicon may explain the preference for O5 to C2 cyclization.

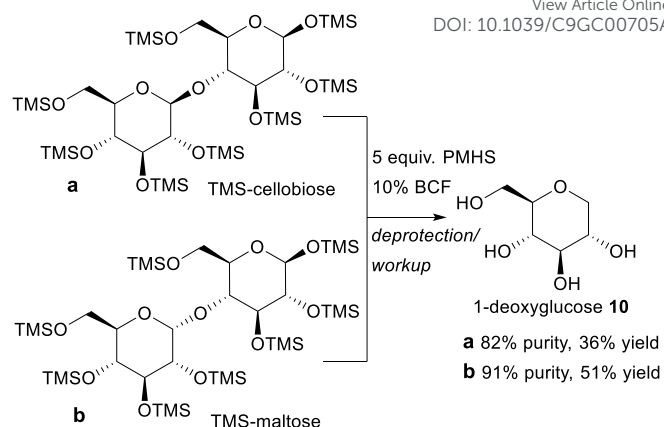


Scheme 6. Proposed mechanism for the production of **8** and **9** from TMS-D-galactose.

anhydrogalactitol **9** after 1 hour (see ESI). Beyond this time, however, the starting material begins to convert to the non-reduced 1,6-anhydrogalactofuranose **8**, eventually generating a near 1:1 ratio of reduced **9** and non-reduced **8**. It appears that the change from a reductive to a non-reductive path is linked to PMHS consumption, but we have been unable to precisely identify the source of this change in reactivity as PMHS is in excess throughout. Considering that the formation of **8** appears to be linked to PMHS consumption, reactivity was probed using more than two equivalents of PMHS. However, at higher equivalencies further reduction of both **8** and **9** occurs, resulting in a complex product mixture with poor control in product selectivity.

To enhance the greenness of the investigated transformations, toluene was tested as an alternative solvent to dichloromethane. Acceptable solvent choices are limited, as oxygenated solvents that could potentially be derived from biomass would interfere with the desired chemistry. Nevertheless, the CHEM21 solvent guide gives toluene a better environmental score compared to dichloromethane and is listed as a “problematic” solvent compared to “hazardous” for DCM.³² TMS-D-glucose was treated with 2.3 equivalents of PMHS monomer (equivalents shown to give good yields of **2** in DCM) with 10% BCF loading in *d*₈-toluene. Under these conditions, reduction to TMS-sorbitol **1** occurred smoothly, with only traces of **2** being observed by in situ ¹³C{¹H} NMR spectroscopy (24 hours). When the equivalents of PMHS monomer were increased to 3.5, **1** still remained the major product, with a slight increase in over-reduced byproducts being observed (see ESI). The change to toluene does lower the kinetic reduction potential, but it also enables a selective protocol to sorbitol.

The disaccharides β-cellobiose and β-maltose were also investigated for their reactivity with polymeric PMHS. Full consumption of TMS-protected disaccharide was achieved using 5.0 equivalents of PMHS per mole of substrate. However, the only isolated product was 1-deoxyglucose **10** (Scheme 7). When the reduction of TMS-cellobiose was investigated using 2.5 equivalents of PMHS per mole of disaccharide, a mixture of starting material, **10**, and TMS-sorbitol **1** was observed in situ by



Scheme 7. Treatment of TMS-cellobiose or TMS-maltose with 5.0 equivalents of PMHS with 10% BCF in DCM yields **10** as the major product.

¹³C{¹H} NMR spectroscopy. While full consumption of disaccharide is achieved with higher equivalents of PMHS, the sorbitol that is produced is also likely deoxygenated to a volatile species, as **1** or products resulting from the further reduction of **1** are absent after deprotection and work-up. The reactivity observed in the case of disaccharide reduction, including the resistance of **10** to further reduction, has been observed by our group previously and is not significantly different from previously reported results.³³

Conclusions

PMHS has been successfully utilized as a greener alternative to traditional hydrosilanes for the reduction and cyclization of carbohydrates to high-value products using metal-free catalysis. The reported reactions are the first examples by which cyclic pyranose sugars can be converted directly to 1,4-anhydro or 2,5-anhydro-products using hydrosiloxane reductants. The cyclization of in situ generated mannitol to 2,5-anhydroglucitol has not been previously observed using a silylium source and is unique to the reactivity of PMHS. These transformations are important contributions to the goal of utilizing renewable resources for the production of fine chemicals.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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