Selective Reduction

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Boron-Catalyzed Regioselective Deoxygenation of Terminal 1,2-Diols to 2-Alkanols Enabled by the Strategic Formation of a Cyclic Siloxane Intermediate**

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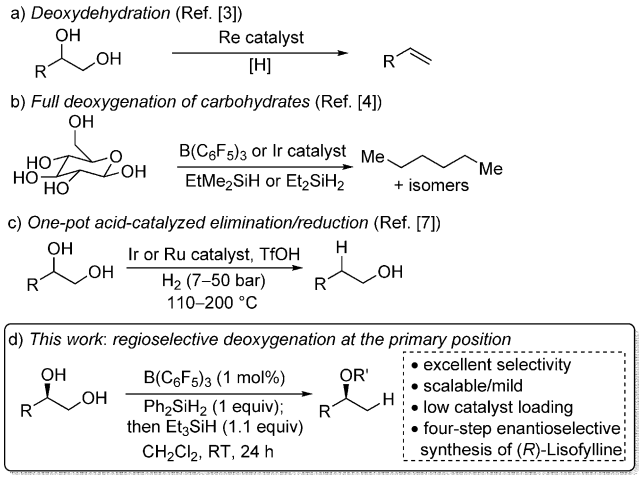
Dedicated to Professor Robert H. Grubbs

Abstract: *The selective deoxygenation of polyols is a frontier in our ability to harness the stereochemical and structural complexity of natural and synthetic feedstocks. Herein, we describe a highly active and selective boron-based catalytic system for the selective deoxygenation of terminal 1,2-diols at the primary position, a process that is enabled by the transient formation of a cyclic siloxane. The method provides an ideal complement to well-known catalytic asymmetric reactions to prepare synthetically challenging chiral 2-alkanols in nearly perfect enantiomeric excess, as illustrated in a short synthesis of the anti-inflammatory drug (R)-lisofylline.*

The deoxygenation of polyols is a critical step in the production of fine chemicals from alcohol-containing feedstocks.[1] A formidable challenge in this area is the predictable and selective deoxygenation of a single alcohol group within an array of hydroxy groups. Such selective deoxygenations of polyols would enable the synthesis of valuable building blocks using starting materials that can be either derived from renewable biomass or prepared by well-established asymmetric catalytic reactions, such as the Sharpless asymmetric dihydroxylation or the Jacobsen hydrolytic kinetic resolution.[2] Herein, we report the first catalytic regioselective deoxygenation of terminal 1,2-diols at the primary position to access 2-alkanols using a simple boron catalyst and commercially available silanes, a process orchestrated by the key formation of a cyclic siloxane intermediate (Scheme 1 d).

Several approaches to the catalytic deoxygenation of polyols have already been reported (Scheme 1). Re-catalyzed deoxydehydration reactions have been developed to efficiently access alkenes from polyols (Scheme 1 a).[3] Another approach to the full deoxygenation of polyols is the catalytic deoxygenation of these substrates using silanes (Scheme 1 b).[4] Inspired by earlier reports describing the efficient deoxygenation of simple alcohols,[5] Gagné and co-workers recently described the complete deoxygenation of carbohydrates using either a boron or iridium catalyst in the presence of silanes.[4] Although these reports (Scheme 1 a and b) are conceptually very interesting approaches to the deoxygenation of renewable feedstocks, they generally do not fully harness the functional and stereochemical complexity of polyols to produce more elaborate, valuable organic building blocks. Therefore, a contemporary challenge of selective catalysis is the invention of novel methods for the partial, selective deoxygenation of polyols.[6]



Scheme 1. Approaches to the catalytic deoxygenation of polyols. R = alkyl group, R′ = H or silyl group.

The regioselective catalytic deoxygenation of terminal 1,2-diols represents an attractive transformation to access valuable 1- and 2-alkanols. In this context, the selective deoxygenation of the secondary alcohol to obtain 1-alkanols has precedent in the literature using both Ir and Ru catalysts and high pressures of H_2 gas (Scheme 1 c).[7] The regioselectivity of these reactions is determined by the formation of the more stable secondary carbocation by trifluoromethanesulfonic acid (TfOH) mediated elimination of water, followed by hydrogenation.[7]

Owing to the lack of catalytic strategies to obtain the reverse selectivity, that is, the more difficult deoxygenation of the primary alcohol, we became interested in inventing such a reaction to transform terminal 1,2-diols into 2-alkanols (Scheme 1 d and Scheme 2 a). As vicinal 1,2-diols are fre-

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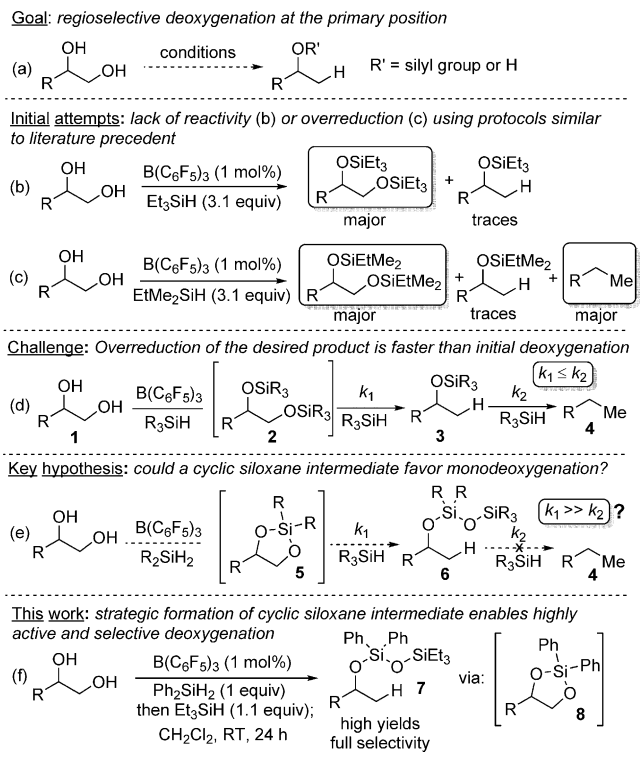
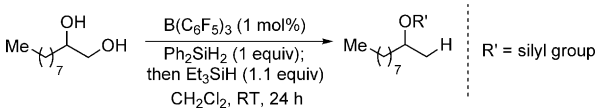


Scheme 2. Initial attempts and design of a new approach. R = alkyl group.

quently encountered in biomass-derived feedstocks, such as carbohydrates, and are easily accessible by known methods in high enantiopurity,[2] the catalytic cleavage of the primary hydroxy group would find applications in the preparation of synthetically challenging 2-alkanols in high enantiomeric excess.[8] 1,2-Decanediol was selected as a test substrate to explore reaction conditions for the regioselective deoxygenation. We targeted the development of Lewis acid catalyzed deoxygenations using commercially available and practical silanes as reducing agents.[9] We were particularly interested in testing the efficiency of simple, commercially available boranes as catalysts to avoid the use of costly transition metals.[10] Unfortunately, preliminary attempts to selectively obtain the desired silylated 2-alkanol using known conditions for alcohol deoxygenations[4,5] did not provide any of the desired product using either Et_3SiH or $EtMe_2SiH$ (Scheme 2b and c).[11] The deoxygenation behavior is critically dependent on the size of the silane. More importantly, the result using no excess of $EtMe_2SiH$ (Scheme 2c) demonstrated experimentally that the second deoxygenation is faster than the initial one when using terminal 1,2-diols (Scheme 2d). This finding can possibly be rationalized by the steric and electronic deactivation of the protected diol intermediate **2** compared to the resulting protected alcohol **3**.[12]

The discouraging lack of desired reactivity in our initial attempts drove us to design a conceptually new approach (Scheme 2e). We hypothesized that the use of a dialkylsilane (R_2SiH_2) in the initial protection step could lead to the transient in situ formation of a cyclic siloxane (**5**). We further reasoned that the formation of this cyclic intermediate would 1) activate the substrate towards initial deoxygenation by decreasing the steric bulk around the oxygen atom, 2) disfavor overreduction of the desired product (**6**) because of the large steric bulk created on the secondary alcohol after the first deoxygenation, and 3) prevent any undesired neighboring group participation. Gratifyingly, this strategy proved successful and led to the development of an extremely active and selective catalytic system for the selective monodeoxygenation of 1,2-diols at the primary position (Scheme 2f and Table 1, entry 1). The intermediacy of the cyclic siloxane **8**

Table 1: Effect of different silanes on the transformation.[a]



Entry	Deviation from the standard conditions	Yield[b] [%]
1	none	86 (79)
2	1 equiv Et_2SiH_2, then 1.1 equiv Et_3SiH	93 (77)
3	no Ph_2SiH_2, 3.1 equiv Et_3SiH	4
4	no Et_3SiH, 2.1 equiv Ph_2SiH_2	0
5	no Ph_2SiH_2, 3.1 equiv Et_2MeSiH	15
6	no Ph_2SiH_2, 3.1 equiv $EtMe_2SiH$	< 5
7	1 equiv Ph_2SiH_2, then 1.1 equiv Et_2MeSiH	76
8	1 equiv Ph_2SiH_2, then 1.1 equiv $EtMe_2SiH$	48
9	5 min interval	28
10	5 min interval, 5 mol% catalyst	81

[a] See the Supporting Information for detailed conditions. [b] Yields determined by ^1H NMR spectroscopy using nitromethane as a standard. Yields of isolated products are given in parentheses.

was confirmed by the incorporation of both silane backbones in the final product (**7**).[13] Table 1 illustrates the critical dependence of the reaction outcome on the nature of the silanes used. Replacing Ph_2SiH_2 by Et_2SiH_2 gave a similar result, although product isolation proved more challenging (entry 2). Using Et_3SiH as the sole silane (entry 3), only traces of the desired product were observed, and the silylated diol was left unreacted. When Ph_2SiH_2 was used alone (entry 4), overreduction was observed, emphasizing the critical interplay of the two silanes under the optimized conditions. Smaller, more reactive silanes (entries 5 and 6) afforded mostly full reduction to decane, with significant amounts of the protected diol left unreacted, even when no excess of silane (3.1 equiv) was used. These results confirmed that the second deoxygenation is faster than the first deoxygenation. A notable size dependence was also observed when different silanes were used after the initial Ph_2SiH_2 addition. Whereas the use of Et_2MeSiH (entry 7) instead of Et_3SiH as the second silane provided a good yield of product, the use of $EtMe_2SiH$ (one Et group switched for a Me, entry 8) led to a much lower yield and significant formation of decane. Finally, when the delay between silane additions was reduced from 4 h to 5 min, the product was formed in low yields, probably because of unselective hydrosilylation (entry 9). However, when the catalyst loading was increased to 5 mol%, the two silanes could be conveniently added with an only 5 min interval, and the product was obtained in good yield (entry 10).

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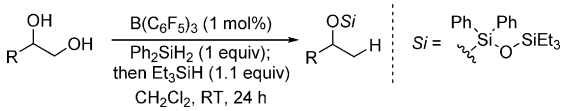
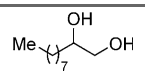
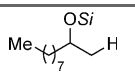
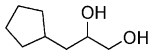
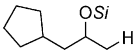
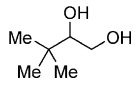
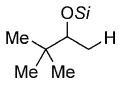
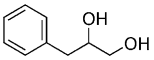
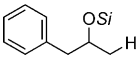
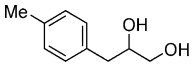
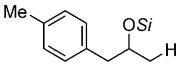
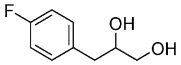
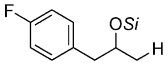
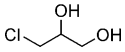
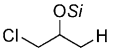
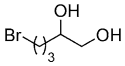
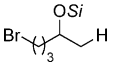
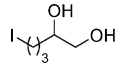
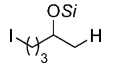
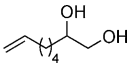
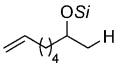
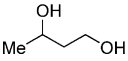
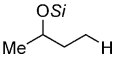
Table 2: Substrate scope.[a]

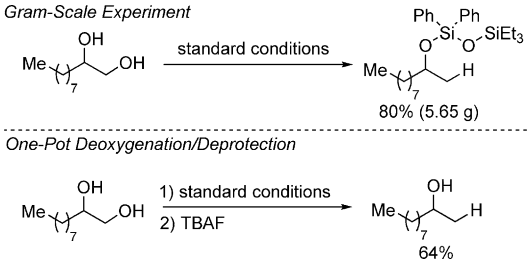


Entry	Substrate	Product	Yield[b] [%]
1			79
2			71
3			69
4			74
5			74
6[c]			62
7			71
8			77
9			51
10			78[d]
11[c]			97

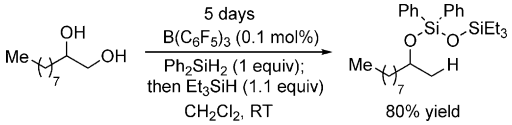
[a] See the Supporting Information for detailed conditions. [b] Yields of isolated products. [c] 5 mol% catalyst. [d] Isolated as a 3:1 mixture, see the Supporting Information.

We next studied the substrate scope and functional group tolerance of the novel transformation (Table 2). Simple aliphatic substrates (entries 1–5) afforded the products in good yield with full regioselectivity. Remarkably, significant steric bulk in close proximity to the diol moiety (entry 3) was also tolerated. Even in transformations of substrates prone to elimination owing to the presence of an aromatic substituent at the vicinal position (entries 4–6), good yields were generally observed. Halogenated substrates were well-tolerated (entries 6–9), even in the case of vicinal substitution (entry 7). These results demonstrate the mild conditions of our reaction system, as alkyl halides are usually prone to reduction in the presence of strong reducing agents.[14] Although the $B(C_6F_5)_3$/Et_3SiH system is known to mediate the hydrosilylation of double bonds under similar conditions,[15] the use of an alkene-containing diol (entry 10) afforded the desired compound as the major product. This result suggests that the deoxygenation of the substrate is significantly faster than the hydrosilylation of the double bond. Finally, the reaction can also be extended to 1,3-diols in excellent yields (entry 11).

The reaction can be readily scaled-up with no loss of efficiency (5.65 g of product, 80% yield; Scheme 3). Whereas the silylated products of the deoxygenation can be conveniently used as protected alcohols in subsequent synthetic steps, we also developed a one-pot procedure that provides



Scheme 3. Scale-up and one-pot deoxygenation/deprotection.

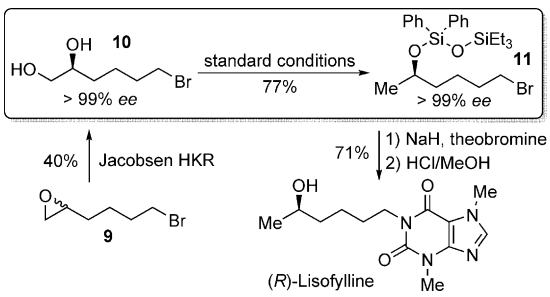


Scheme 4. Experiment with low catalyst loading.

direct access to the free alcohol in 64% yield using tetrabutylammonium fluoride (TBAF; Scheme 3).

When the catalyst loading was reduced to 0.1 mol% and the reaction time increased, the product was also obtained in good yield (Scheme 4). Previously, catalyst loadings between 5 and 10 mol% were usually required for the efficient deoxygenation of alcohols.[16]

Finally, we envisaged that our novel method could be applied to the preparation of enantioenriched 2-alkanols, which are challenging to access in high enantiomeric excess by the asymmetric hydrogenation of ketones because of the difficulty for the hydrogenation catalysts to differentiate between the two prochiral faces of ketones bearing substituents of similar size.[17] We thus reasoned that when combined with established methods to access terminal diols in high enantiopurity, our deoxygenation reaction could be used to obtain useful 2-alkanols in nearly perfect enantiopurity.[18] The retention of chiral information at the secondary alcohol during the deoxygenation step was therefore evaluated (Scheme 5). We subjected chiral bromodiol **10**, which was synthesized by the Jacobsen hydrolytic kinetic resolution in >99% *ee*, to our standard reaction conditions and obtained the protected alcohol **11** in >99% *ee*, with full retention of stereochemistry. The silyl group introduced in the deoxyge-



Scheme 5. Conservation of enantiopurity and synthesis of (*R*)-lisofylline. HKR = hydrolytic kinetic resolution. See the Supporting Information for details.

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nation step can conveniently act as a protecting group, and enantiopure **11** could thus be used directly in a one-pot synthesis of (*R*)-lisofylline, an anti-inflammatory drug that has also shown promising anti-diabetes activity.[19]

In conclusion, we have described the first catalytic, selective monodeoxygenation of terminal 1,2-diols at the primary position. The reaction proceeds in good yields using a combination of two silanes and a commercially available boron catalyst. The method exhibits good functional group compatibility with no excess of silanes, can be run at low catalyst loading (as low as 0.1 mol%), is amenable to gram-scale synthesis, and can be used to prepare challenging enantioenriched 2-alkanols. In a broader context, we believe that the observations made during this study, namely that the selectivity and reactivity of the deoxygenation can be dramatically improved by the strategic formation of a cyclic siloxane intermediate, will guide the development of new and selective transformations of complex polyols.

Keywords: boron · cyclic intermediates · deoxygenation · diols · silanes

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Angew. Chem. **2015**, *127*, 8938–8942

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