Rhenium-Catalyzed Didehydroxylation of Vicinal Diols to Alkenes Using a Simple Alcohol as a Reducing Agent

Elena Arceo, Jonathan A. Ellman,* and Robert G. Bergman*

Department of Chemistry, University of California, and Division of Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Received April 22, 2010; E-mail: jonathan.ellman@yale.edu; rbergman@berkeley.edu

Abstract: A new method for the catalytic didehydroxylation of vicinal diols is described. Employing a readily available low-valent rhenium carbonyl complex and a simple alcohol as a reducing agent, both terminal and internal vicinal diols are deoxygenated to olefins in good yield. The optional addition of acid (TsOH, H_2SO_4) provides access to lower reaction temperatures. This new system enables the transformation of a four-carbon sugar polyol into an oxygen-reduced compound, providing promising evidence for its practical application to produce unsaturated compounds from biomass-derived materials.

The development of new synthetic technologies for the production of reduced oxygen-content materials from renewable biomass resources is a key target in chemistry and chemical engineering research.[1] Our group is exploring new routes to deoxygenate biomass-derived polyols,[2] and the didehydroxylation of diol moieties is an important goal in this context. Various stoichiometric methods for carrying out diol didehydroxylation are synthetically valuable,[3] but catalytic methods are rare.[4] In particular, didehydroxylation has been achieved using $Cp*ReO_3$ as a catalyst, although triphenylphosphine was needed as a sacrificial reductant.[4a] We report herein a catalytic method for the didehydroxylation of vicinal diols to alkenes that employs a readily available low-valent rhenium carbonyl complex and a simple alcohol as an environmentally friendly reducing agent.

During preliminary experiments, we observed that heating (4S*,4S*)-octane-4,5-diol (**1**) at 180 °C in solvent-free conditions, under air and in the presence of dirhenium decacarbonyl (**3a**, 2.5 mol %), resulted in complete consumption of **1** in 3.5 h to yield the olefin **2** in 50% yield as determined by NMR spectroscopy (Scheme 1). A droplet of phase-separated water was also detected in the reaction mixture.

Aliquots of the mixture from the reaction of diol **1** and **3a** at intermediate conversion contained the vicinal diketone **4** (as identified by ^{1}H, ^{13}C NMR spectroscopy and MS). Although at the early stages of the reaction the amount of **4** increased along with the formation of **2**, its depletion was subsequently observed leading to its disappearance when complete conversion of **1** was achieved (vicinal diketones are unstable under the reaction conditions; see Supporting Information (SI)). These results suggested that the transformation might occur through a disproportionation reaction in which the diol (**1**) is reduced to generate an alkene (**2**) and concurrently acts as a reductant to give oxidized products (**4**).

Similar results were observed when the terminal diol 1,2-tetradecanediol (**5**; see Table 1) was submitted to the same reaction conditions, in which the yield of 1-tetradecene (**6**) was determined to be 49% (isolated). The diols remained unchanged when heated in the presence of **3a** under air at temperatures lower than 170 °C. When the experiment was conducted in the absence of O_2 (N_2 atmosphere) no reaction was observed after heating at 180 °C for extended periods (24 h).

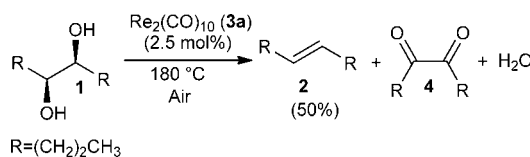**Scheme 1.** Disproportionation of Diol **1** Catalyzed by $Re_2(CO)_{10}$

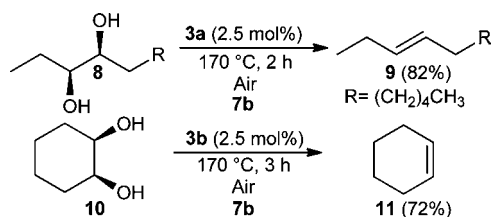**Table 1.** Rhenium-Catalyzed Didehydroxylation of Diol **5** Using Alcohol **7a**, **b**, or **c** as a Reductant

entry[a]	catalyst	reductant (mL)	temperature (°C)	time (h)	yield **6**[b] (%)
1	**3a**	**7a** (4)	180	3.5	83
2	**3a**	**7b** (4)	170	4	82 (82)
3	**3a**	**7b** (5)[c]	170	4	83
4	**3a**	**7c** (4)	170	3.5	74
5	**3b**	**7b** (4.5)	170	4	84 (85)

[a] Reactions conducted at 2.5 mmol scale under air. Details in SI. [b] Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. Isolated yield in parentheses. [c] Further increase in the volume of reductant resulted in longer reaction times without any significant improvement in yield.

As this system is able to use a vicinal diol as both oxidant and reductant, we hypothesized that adding a simple alcohol as a reductant[5] might enable selective conversion of the diol moiety to a C−C double bond without competing diol oxidation. We chose 1,2-tetradecanediol (**5**) as a substrate for optimization due to the low volatility of the possible products. When the reaction of **5** (2.5 mmol) and **3a** (2.5 mol %) was performed at 180 °C under air and in the presence of 5-nonanol (**7a**)[6] (9 equiv), the yield of the alkene was enhanced to over 80% (Table 1, entry 1).

Other high-boiling alcohols such as 3-octanol (**7b**) and 2-octanol (**7c**) also gave enhanced yields of the desired product (entries 2−4, Table 1). The use of 9 to 13 equiv of reductant afforded complete conversion of **5** in 3.5 to 4 h. In this process, the alcohols **7a**−**c** generated 1 to 1.5 equiv of the corresponding ketone. We briefly investigated the use of other low-valent rhenium complexes; while $Cp*Re(CO)_3$ did not show any activity, $BrRe(CO)_5$ (**3b**) exhibited behavior similar to that observed with **3a** (entry 5).

The use of an alcohol as a reductant also resulted in improved yields for internal diols. For example, (3R*,4R*)-decane-3,4-diol (**8**, 2.5 mmol) afforded the alkene **9** in 82% yield after 2 h at 170 °C in 3-octanol (4.5 mL) with 2.5 mol % of **3a** (Scheme 2). The cyclic diol *cis*-1,2-cyclohexanediol (**10**) also provided the corresponding olefin (**11**) in good

Scheme 2. Rhenium-Catalyzed Didehydroxylation of the Internal Diols **8** and **10** Using 3-Octanol as a Reductant

Table 2. Effect of *para*-Toluenesulfonic Acid (**T**) and Sulfuric Acid (**S**) as Additives in the Rhenium-Catalyzed Didehydroxylation of **5**[a]

entry	3a (mol %)	7b (mL)	acid (mol %)	temp (°C)	time (h)	conv (%)	yield[b] 6 (%)
1	2.5	4	−	155	5	0	0
2	2.5	4	T (5)	155	2.5	100	74(76)
3	1	3	−	170	16	80	46
4	1	3	T (2)	155	1.5	100	77
5	1	5	T (2)	155	1.8	100	87(83)
6	2.5	5	S (2)	155	2	100	82(85)
7	1.25	5	S (2)	155	2	100	79

[a] Reactions conducted at 2.5 mmol scale under air. Details in SI. [b] Determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. Isolated yield in parentheses.

yield. Conversely, the stereoisomer *trans*-1,2-cyclohexanediol did not react in the presence of the alcohol or in solvent-free conditions.

In an attempt to decrease the reaction temperature, the use of an additive was investigated. This is relevant from the perspective of the application to sugar polyols, since these materials tend to decompose at high temperatures. The presence of bases such as tri-*n*-hexylamine or K_2CO_3 resulted in longer reaction times or total obstruction of reactivity (Table S2, Supporting Information). Conversely, the presence of catalytic quantities of *para*-toluenesulfonic acid (TsOH) or sulfuric acid not only shortened the reaction times but also permitted the reaction to proceed at lower temperatures and with lower catalyst loading.

Heating a mixture of **5**, **3a**, and **7b** (1: 0.025: 10) at 155 °C in the presence of 5 mol % of TsOH resulted in complete conversion of **5** in 2.5 h (entry 2, Table 2, compare to entry 1). Lowering the concentration of TsOH (2 mol %) and catalyst (1 mol %) resulted in complete conversion in 1.5 h at 155 °C (entry 4, compare to entry 3). By increasing the amount of reductant to 12.6 equiv and using 1 mol % of **3a**, **6** was obtained in 87% yield in less than 2 h at 155 °C. The presence of catalytic quantities (2 mol %) of H_2SO_4, one of the most widely used industrial chemicals, resulted also in good yields of the olefin at 155 °C, even with catalyst loadings as low as 1.25 mol % (entries 6, 7). The reaction did not proceed in the absence of **3a** in the presence of catalytic quantities of H_2SO_4 or TsOH.

In order to investigate the scope of this reaction in the context of biomass-derived materials, *meso*-erythritol (**12**), a four-carbon sugar-derived polyol, was selected as a starting material in a first step toward more complex substrates. Our preliminary results are very promising, in view of the fact that 2,5-dihydrofuran (**13**) was formed (62% NMR yield) under the relatively mild conditions depicted in Scheme 3. Product **13** was isolated (55% yield; >94 mol % pure) by fractional distillation from the crude reaction mixture. We believe that the presence of the acid additive in the mixture favors the initial cyclization of erythritol to 1,4-anhydroerythritol,[2] which then undergoes didehydroxylate in the presence of **3a** and reductant to afford the final reduced oxygen-content product.

Scheme 3. Rhenium-Catalyzed Deoxygenation of Erythritol
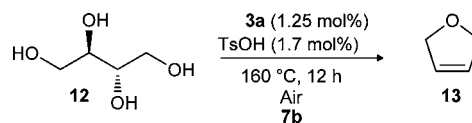
In contrast to the simplicity of the reaction methodology, the mechanism of the reaction is still unknown. The manifest temperature and oxygen dependence of this transformation suggests an oxidized rhenium species as the active catalyst, and the requirement that the diol be capable of achieving a *cis* disposition for the reaction to proceed is consistent with the intermediacy of a rhenium diolate species. Some metal diolates are known to extrude the corresponding alkene on thermolysis.[7] Stoichiometric extrusion of olefins has been reported from high-oxidation-state organorhenium oxides, for example Re(VII)[8] and Re(V),[9] and is believed to be operative in the Cp*ReO₃-catalyzed reaction mentioned previously.[4a] Unlike that system, the present method tolerates alcohols as reductants and can be performed in the presence of oxygen which suggests a qualitative difference in the reaction mechanism. We hypothesize that the significant effect of the presence of acid on the catalyst performance might be related to an assisted olefin extrusion by protonation of a rhenium diolate intermediate.

In conclusion, these results provide a new catalytic system based on a rhenium-mediated didehydroxylation of vicinal diols using a simple alcohol as reductant. The addition of acid provides access to milder reaction temperatures. The practical application to erythritol strongly suggests that this chemistry could be used to produce unsaturated compounds from other biomass-derived polyols. Further studies of the mechanism and investigation of other substrates and additives are in progress.

Supporting Information Available: Additional information, tables, and experimental procedures with figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA103436V