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Rhenium-catalyzed deoxydehydration of renewable biomass using sacrificial alcohol as reductant

Justin Gossett, Radhey Srivastava *

Department of Chemistry, University of Louisiana at Lafayette, Lafayette, LA 70504, USA

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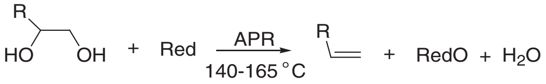
ABSTRACT

Catalytic deoxydehydration (DODH) of vicinal diols is studied. We find that NH_4ReO_4 (ammonium perrhenate, APR) catalyzes the DODH of glycols to alkenes by sacrificial alcohol (2,4-dimethyl-3-pentanol) at 140–165 °C. The product yields range from good to excellent and no isomers detected. The catalytic DODH reaction of glycols to alkene is of potential value for the production of chemicals and fuels from the renewable biomass-derived polyols.



Introduction

The biomass contains abundant hydroxyl groups, which is found in both carbohydrates (obtained from cellulose, hemicellulose, and starch) and glycerol (obtained from triglycerides). The strategy is to reduce oxygen content from biomass to produce diverse classes of value-added chemicals. Initial efforts were focused on dehydration[1] and deoxydehydration (DODH)[2] processes; significant advances accomplished with both, dehydration and DODH processes. To develop a proficient process for the conversion of renewable biomass into reduced oxygen-content products (fuels and value-added chemicals) has fascinated increased attention with the growing demand for sustainability.[3,4] Recent research interest has focused on selective oxygen removal through deoxydehydration (DODH), in which vicinal hydroxyl groups removed to form olefin (Scheme 1). The olefins obtained from DODH reactions are valuable and have diverse applications in the manufacture of chemical intermediates such as polymers and lubricants.

The first report on DODH was disclosed by Andrews and Cook[5] using (C_5Me_5) ReO_3 catalyst in the presence of phosphine reductants (Scheme 1). A valued contribution discloses by Gable et al.[6] vis-à-vis mechanism of DODH reaction catalyzed by (trispyrazolylborate) ReO_3 in the presence of phosphine as reductant. Lately, significant advances have been achieved using more economical and benign reductant for DODH reaction. The high valent oxorhenium complexes have been used for DODH reaction employing a variety of reductants such as H_2[7] and Na_2SO_3.[8] Afterwards various research groups developed Re-catalyzed DODH of vicinal diols[9] in the presence of primary, benzylic, and secondary alcohols as reductants. Sacrificial alcohols have been widely used as effective reductants for the conversion of glycol to olefin in the presence of rhenium-based catalysts.

The Bergman group established a hydrogen-transfer type DODH reaction catalyzed by $[Re_2(CO)_{10}]$ and $[BrRe(CO)_5]$ in conjunction with a secondary alcohol as solvent/reductant.[10] The Toste group demonstrated the efficient conversion of higher polyols by secondary alcohols to form unsaturated alcohols, unsaturated ethers, and polyenes (as well as the associated ketones) in the presence of $MeReO_3$ (MTO) catalyst.[11] Further, Abu Omar and Liu reported the MTO-catalyzed redox disproportionation of glycerol to allyl alcohol, acrolein, and propanal, which can be distilled. In addition to distillable product, they also obtained nonvolatile dihydroxyacetone.[12] Hydroaromarics have also been established as effective reductant for the glycol deoxydehyration in the presence of Re-cat-

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* Corresponding author.
E-mail address: rss@louisiana.edu (R. Srivastava).

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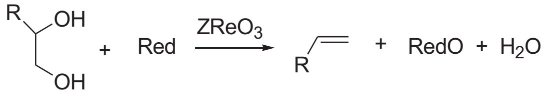
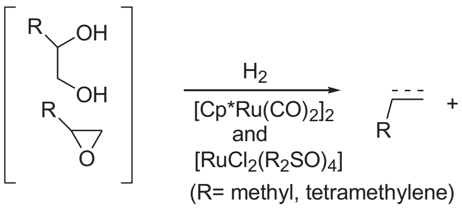


Scheme 1. Metal-catalyzed DODH reaction.



Scheme 2. $[Cp^{*}Ru(CO)_2]_2$-catalyzed hydrodeoxygenation and hydrocracking and $RuCl_2(R_2SO)_4$-catalyzed hydrogenolysis of diols and epoxides (R = methyl and tetramethylene).

alyst.[13] $[Cp{*}Ru(CO)_2]_2$-catalyzed hydrodeoxygenation and hydrocracking and $RuCl_2(R_2SO)_4$-catalyzed hydrogenolysis of diols and epoxides has also been established by us (Scheme 2).[14,15]

The Nicholas group[9c] have used ammonium perrhente (APR) catalyst for the DODH reaction of vicinal diols in the presence of benzylic alcohol as reductant. In the pursuit to develop a new DODH processes for the conversion of renewable cellulosic biomass to valuable chemicals, we revisited the chemistry of NH_4ReO_4 and developed a modified process, which requires a small amount of secondary alcohol (4.28×10^{-4} to 8.56×10^{-4} mol) as a reductant compared to earlier reports[9b,c] (Scheme 3). The reaction is clean and no byproducts except the oxidized byproduct of 2,4-dimethyl-3-pentanol detected.

Experimental section

General information

All reagents were obtained commercially and used without further purification. All solvents were ACS grade and were used directly (unless otherwise described in the procedures). GC–MS analyses were performed on an Agilent instrument using a Stabilwax capillary column. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard for ^1H (Varian, 400 MHz) and for ^{13}C (100 MHz) spectra.

Typical reaction procedure

Glycerol (0.3 mmol, 42 mg), NH_4ReO_4 (0.03 mmol, 8 mg), 2,4-dimethyl-3-pentanol (0.43–0.86 mmol, 60–120 µL), and 1 mL anhydrous toluene were added to a thick-walled Ace glass reactor tube. The Teflon seal was closed and the reactor was placed in a heating mantle connected with a Digi Troll (Glas-Col) digital temperature controller equipped with a thermocouple at 140-165 °C for 5–48 h while stirring. After cooling to room temperature, the solution was filtered to remove the precipitated NH_4ReO_4 and analyzed with GC–MS.

Table 1
Optimization of solvents and alcohol reductants in the presence of NH_4ReO_4 catalysts.

Entry	Solvent	Styrene (%)	Time (h)
1	Toluene	84	4
2	Toluene	99	5
3	1-Butanol	42	24
4	Benzene	17	24
5	THF	32	24
6	Acetonitrile	19	24
7	3-Octanol	75	24
8	Isopropanol	10	24

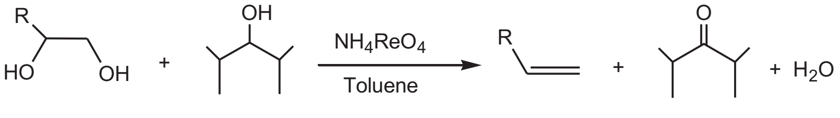
Isolation

NH_4ReO_4 (28 mg, 0.1 mmol,), (+)-diethyl tartrate (198 mg, 1 mmol), 2,4-dimethyl-3-pentanol (388 µL), and anhydrous toluene (6 mL) were added to a thick-walled Ace glass reactor tube. The reactor was placed in a heating mantle bath in the range of 165 °C for 24 h while stirring magnetically. The reaction mixture was cooled and filtered over silica gel. Solvents were removed using a rotary evaporator under reduced pressure. The product was separated by column chromatography using ethyl acetate/hexane eluent. Product yield was 73 mg, 42%.

Result and discussion

In pursuit to improve catalytic systems for DODH with better efficiency, we prefer to use ionic ammonium perrhenate (APR, NH_4ReO_4) as a suitable catalyst. APR is inexpensive, known for DODH ability, greater hydrolytic stability compared to $MeReO_3$,[16] and its ionic nature. To test the viability of alcohols as a reductant for the DODH of glycols, an exploratory reaction was carried out with styrene diol, 2,4-dimethyl-3-pentanol and ammonium perrhenate (10 mol%) in anhydrous toluene, which produced styrene quantitatively in 5 h at 165 °C. We began the survey with polar and apolar solvents at various temperatures. The reaction performed in anhydrous toluene produced an excellent yield of the alkene whereas hydrated toluene and benzene resulted in a low yield. The addition of 4 Å molecular sieve did not change the product yield. The coordinating solvent such as THF and acetonitrile also produced significantly lower yield of styrene, probably due to the coordination of solvent to Re (Table 1). Our next step was to screen the effect of temperature and we found that 160–165 °C was the optimum temperature for the model substrate for optimum yield of alkene. We preferred secondary alcohol (2,4-dimethyl-3-pentanol) over butanol-1,3-octanol, and isopropanol for DODH reductant because the higher yiled of alkenes and the resulting ketone co-product could be easily separated from the olefinic products in GC–MS.

After optimizing reaction conditions (10 mol% APR, 0.3 mmol glycol, 2,4-dimethyl-3-pentanol in anhydrous toluene, 140-165 °C, 4–24 h), we determined that the representative glycols were converted to the corresponding olefins in good to excellent yields (Scheme 3, Table 2). All polyols subjected to catalytic reaction are efficiently converted to the corresponding alkenes regioselectivily as is shown in Table 2. The activated diol such as 1-phenyl-1, 2-ethanediol converted to styrene quantitatively in 5 h at 165 °C (run 1, Table 2). Long chain diols, tetradecanediol



Scheme 3. Optimized DODH reaction scheme for glycol conversion to the corresponding olefins.

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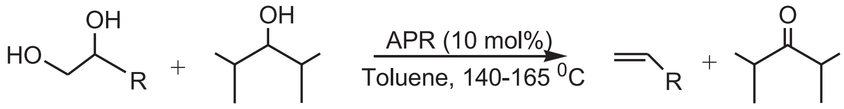
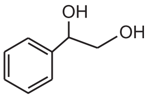
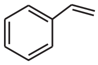
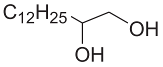
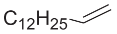
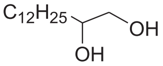
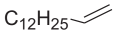
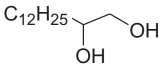
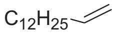
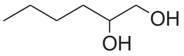
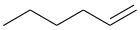
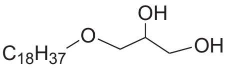
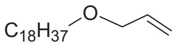
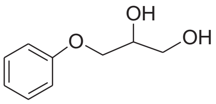
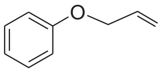
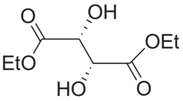
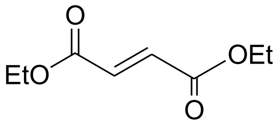
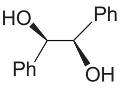
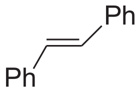
Table 2
APR-catalyzed DODH of glycols in the presence of 3,4-dimethyl-3-pentanol reductant.



Entry	Glycol	Alkene	T (°C)	Time (h)	Yield (%)[a,b,c]
1			165 165	4 5	84 99
2			165	25	50
3			150	5	36[c]
4			150	24	99[c]
5			165	24	9
6			140	24	73
7			140	48	90
8			140	24	57 (42)
9			165	24	60 (48)

[a] Conversion and yield determined by gas chromatography (GC) using dodecane as the internal standard.
[b] Isolated yields are given in parentheses.
[c] 3-Octanol was used as reductant.

(run 2, Table 2) is active and give corresponding alkene in 50% yield in 25 h at 165 °C. Tetradecaediol in the presence of 3-ocatanol as reductant produced 1-octene in 36% in 5 h and 99% in 24 h (run 3, 4, Table 2). However, 1, 2-hexanediol (run 5, Table 2) is very sluggish and produces only 9% hexene. However, no reaction with *trans*-cyclohexanediol was detected. In order to check the functional group tolerance, we examined diols containing functional groups and found that the acid and water-sensitive ether linkage is well tolerated. Thus batyl alcohol (run 6, Table 2) and 3-phenoxy-1,2-propoanediol (run 7, Table 2) that has ester linkage converted into corresponding alkenes with good to excellent yield. The stereoselective conversion of (+)-diethyl tartrate and (*R*, *R*)-(+)-hydrobenzoin to diethyl fumarate and *trans*-stilbene respectively (runs 8 and 9, Table 2) proceeded stereoselectively. The conversion of diethyl tartrate to diethyl fumarate and no product formation from *trans*-cyclohexanediol indicate a *syn*-diol elimination, consistent with a concerted fragmentation of the presumed Re-glycolate intermediate.

Conclusion

In summary, ionic ammonium perrhenates have been shown to be catalysts for the deoxydehydration of glycols in the presence of small amounts of sacrificial alcohol (2,4-dimethyl-3-penatnol) as reductant. The APR is effective with 2,4-dimethyl-3-pentanol as reductants, producing olefinic products regio- and stereoselectively and in good yield.

Acknowledgements

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