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# Oxorhenium-catalyzed deoxydehydration of glycols and epoxides

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#### ARTICLE INFO

### ABSTRACT

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#### Introduction

The growth of effective procedures for the synthesis of reduced oxygen-content products from cellulosic biomass is an important step toward the practical utilization of renewable resources to produce fuels and valuable chemicals.<sup>1,2</sup> Discerning homogeneous (Cp\*Ru(CC)LH) and heterogeneous (Ru-C) catalyzed monodehydroxylation of glycols has been realized via hydrogenolysis.<sup>3,4</sup> The use of hypervalent oxorhenium complexes for deoxydehydration (DODH) employing various reductants such as PPh<sub>3</sub>,<sup>5</sup> H<sub>2</sub><sup>6</sup> and Na<sub>2</sub>SO<sub>3</sub><sup>7</sup> are well known. The Bergman group established a hydrogen-transfer-type DODH reaction catalyzed by [Re<sub>2</sub>(CO)<sub>10</sub>] and [BrRe(CO)<sub>5</sub>] in conjunction with a secondary alcohol as solvent and reductant.<sup>8</sup> Fernandes et al. have demonstrated oxorheniumcatalyzed DODH of styrene oxides in the absence of reductant.<sup>9</sup> A recent report from the Sen group<sup>10</sup> demonstrated the practicability of a one-step rhodium-catalyzed process for the production of THF derivatives for liquid fuels from carbohydrates and cellulosic biomass. Oxorhenium-catalyzed deoxygenation of sugars and sugar alcohols has been reported lately by Toste.<sup>11</sup> This group reported that glycerol, a by-product of biodiesel (fatty acid esters) was transformed to allyl alcohol in 90% yield.<sup>11</sup> Likewise, a C<sub>4</sub> alcohol sugar such as erythritol (obtained by the fermentation of glucose<sup>12</sup> or by the decarbonylation of pentoses)<sup>13</sup> was converted into 1,3-butadiene, an industrially important rubber precursor. The pincer complex, IrH<sub>2</sub>(POCOP)

The conversion of renewable cellulosic biomass into hydrocarbons has attracted significant attention with a growing demand of sustainability. MeReO<sub>3</sub> catalyzes the deoxydehydration (DODH) of glycols and epoxides to alkenes by primary and secondary alcohols (5-nonanol, 3-octanol, 1-butanol) in the benzene solvent. The product yield range from moderate to excellent.

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 $[POCOP = \eta^3 - C_6H_3 - 1, 3 - (OP(^tBu)_2)_2]$  was employed in the partial hydrogenolysis of 1,2-propanediol to n-propanol under mild conditions in acidic aqueous dioxane.14

We recently reported the [Cp\*Ru(CO)<sub>2</sub>]<sub>2</sub>-catalyzed hydrodeoxygenation and hydrocracking and RuCl<sub>2</sub>(R<sub>2</sub>SO)<sub>4</sub>-catalyzed hydrogenolysis of diols and epoxides<sup>15</sup> (Scheme 1).

In the quest to develop new and cheaper DODH processes, at least in part, for the conversion of renewable cellulosic biomass into valuable chemicals we revisited the chemistry of MeReO<sub>3</sub> and developed a modified process which requires a small amount of a primary or secondary alcohol as a reductant compared to earlier reports.<sup>8,11</sup>

#### **Results and discussion**

During our experiments, 1-phenyl-1,2-ethanediol (styrenediol), a prototypical substrate was examined for reactivity with small amounts of a secondary alcohol such as 5-nonanol, 3-octanol, and 1-butanol ( $6.8 \times 10^{-4}$  mol) in the presence of MeReO<sub>3</sub> (MTO)



Scheme 1. [Cp\*Ru(CO)<sub>2</sub>]<sub>2</sub>-catalyzed hydrodeoxygenation and hydrocracking and RuCl<sub>2</sub>(R<sub>2</sub>SO)<sub>4</sub>-catalyzed hydrogenolysis of diols and epoxides (R = methyl and tetramethylene).

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## **ARTICLE IN PRESS**

J. Davis, R. S. Srivastava/Tetrahedron Letters xxx (2014) xxx-xxx

Scheme 2. Re-catalyzed deoxydehydration of styrenediol to styrene.

**1** and benzene solvent. (Scheme 2) The reaction between the glycol and 5-nonanol was first conducted in benzene with 10 mol % MTO in a thick-walled sealed glass tube at 90 °C, resulting in the quantitative conversion of styrene diol into styrene (97%) (Table 1, entry 1). To understand the mechanism of ruthenium-catalyzed deoxy-dehydration, we examined the catalyst activity as a function of dependence on the solvent, temperature, and reductant. Thus in the presence of toluene and THF, 34% (in toluene) and trace amount (in THF) of styrene was detected. On the examination of the reaction rate at 110 and 200 °C, styrene was obtained in 80% and 56%, respectively (Table 1, entries 2 and 3). Likewise, in the presence of the reductant 3-octanol styrene was produced in 35% and 1-butanol produced 22% styrene. We also examined the reactivity of another rhenium catalyst, [Re(CO)<sub>10</sub>], which only gave trace amounts of styrene and phenyl ethyl alcohol.

Glycols which may be better models for biomass-derived products were also examined in the Re-catalyzed DODH reaction in order to determine the products' selectivity and efficiency (Table 1). When subjected to the reaction conditions (140 °C, 0.687 mmol 5nonanol and 10 mol % 1), 1,2-hexanediol produced hexene in 10% yield in 48 h (Table 1, entry 4) as the only detected product by GC–MS. No products were detected at lower temperatures. The

Table 1



Scheme 3. Plausible mechanistic pathway of Re-catalyzed deoxydehydration of glycols.

long chain 1,2-tetradecanediol was even less reactive, with no hydrocarbons being detected at a low temperature. However, when this reaction was conducted at 150 °C, tetradecene (50%) and two other isomeric alkenes of same molar mass (5% and 8%) were produced after 95 h (Table 1, entry 5). In contrast, the cyclic glycol, *cis*-1,2-cyclohexanediol was converted into cyclohexene (15%), with no detectable alkane or cracking products (Table 1, entry 6). When 1,4-anhydroerythritol (a biomass-derived glycol) was treated under same reaction conditions, it afforded 3-tetrahydrofuranol in low yield (10%) (Table 1, entry 7).

Re-catalyzed deoxydehydratic	on of glycols and epoxides <sup>a</sup>



<sup>a</sup> 0.36 mmol glycol in benzene (2 mL), 0.036 mmol MeReO<sub>3</sub>, 5-nonanol (0.68 mmol) 90 °C; yields determined by GC–MS with *n*-dodecane as internal standard.

<sup>b</sup> Other possible isomeric alkenes observed in low yields.

The DODH of epoxides catalyzed by **1** was also examined. Thus, styrene oxide was converted quantitatively into styrene (99%) (Table 1, entry 8), the same product (styrene) was formed from the corresponding glycol. Similarly, cyclohexene oxide afforded cyclohexene in 54% yield after 24 h at a high temperature (Table 1, entry 9), again with no alkane detected. 1,2-Hexene oxide (like the corresponding glycol) was converted into 2-hexene in 17% yield (Table 1, entry 10).

The catalytic pathways for the DODH reactions promoted by **1** are unclear at present. The similar product profiles in both the glycol and epoxide deoxydehydration suggest the involvement of common intermediates. Based on our observation and literature reports<sup>6,11</sup> we believe that the mechanism for glycols would be similar to the one proposed by Toste et al.<sup>11</sup> We have shown the mechanism for the epoxides in Scheme 3. MeReO<sub>3</sub> (**1**) reacts with alcohol to generate Re(V)-dioxide (**2**) to which epoxide would coordinate and form Re(V)-glycolate (**4**) followed by generation of alkene and MeReO<sub>3</sub>(**1**). The validity of Re(VII)-glycolate is supported by the known reversible condensation of **1** with glycol.<sup>6,16,17</sup> Formation of truncated alkenes in the present system can also be explained by the intermediacy of a metallogycolate species (Scheme 2).<sup>15</sup>

In conclusion, we report here a modified system for glycol and epoxide conversion into alkenes using primary and secondary alcohols (1-butanol, 5-nonanol, and 3-octanol) as reductant and MeReO<sub>3</sub> as a pre-catalyst. Future investigations will focus on elucidating the important catalytic species and mechanisms of these reactions and their application to biomass-derived polyols.

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#### Supplementary data

Supplementary data (experimental procedure and spectral data for compounds) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.05.044.

#### References

- (a) Huber, G. W.; Iborra, S.; Corma, A. Chem. Rev. 2006, 106, 4044; (b) Corma, A.; Iborra, S.; Velty, A. Chem. Rev. 2007, 107, 2411.
- (a) Sharpless, K. B.; Umbreit, M. A.; Nieh, M. T.; Flood, T. C. J. Am. Chem. Soc. 1972, 94, 6538; (b) Corey, E. J.; Hopkins, P. B. Tetrahedron Lett. 1982, 23, 1979; (c)Comprehensive Organic Transformations: A Guide to Functional Group Preparations; Larock, R. C., Ed.; VCH: New York, 1993.
- Schlaf, M.; Ghose, P. J.; Hauptman, E.; Bullock, R. M. Adv. Synth. Catal. 2009, 351, 789.
- (a) Deng, W.; Tan, X.; Fang, W.; Zhang, Q.; Wang, Y. Catal. Lett. 2009, 133, 167;
  (b) Yan, N.; Zhao, C.; Luo, C.; Dyson, P. J.; Liu, H.; Kou, Y. J. Am. Chem. Soc. 2006, 128, 8714.
- 5. Cook, G. K.; Andrews, M. A. J. Am. Chem. Soc. 1996, 118, 9448.
- Ziegler, J. E.; Zdilla, M. J.; Evans, A. J.; Abu-Omar, M. M. Inorg. Chem. 2009, 48, 9998.
- (a) Vkuturi, S.; Chapman, G.; Ahmad, I.; Nicholas, K. M. Inorg. Chem. 2010, 49, 4744; (b) Ahmad, I.; Chapman, G.; Nicholas, K. M. Organometallics 2011, 30, 2810.
- 8. Arceo, E.; Ellman, J. A.; Bergman, R. G. J. Am. Chem. Soc. 2010, 132, 11408.
- 9. Sousa, S. C. A.; Fernandes, A. C. Tetrahedron Lett. 2011, 52, 6960.
- 10. Yand, W.; Sen, A. ChemSusChem 2010, 3, 597.
- 11. Shiramizu, M.; Toste, F. D. Angew. Chem., Int. Ed. 2012, 8082.
- 12. Koh, E.-S.; Lee, T.-H.; Lee, D.-Y.; Kim, H.-J.; Ryu, Y.-W.; Seo, J.-H. Biotechnol. Lett. 2003, 25, 2103.
- 13. Monrad, R. N.; Madsen, R. J. Org. Chem. 2007, 72, 9782.
- (a) Foskey, T. J. A.; Heinekey, D. M.; Goldberg, K. I. ACS Catal. 2012, 2, 1285; (b)
  Williams, C. L.; Chang, C.-C.; Do, P.; Nikbin, N.; Caratzoulas, S.; Vlachos, D. G.; Lobo, R. F.; Fan, W.; Dauenhauer, P. J. ACS Catal. 2012, 2, 935.
- (a) Stanowski, S.; Nicholas, K. M.; Srivastava, R. S. Organometallics 2012, 31, 515; (b) Murru, S.; Nicholas, K. M.; Srivastava, R. S. J. Mol. Catal. A 2012, 364– 365, 460.
- 16. Zhu, Z.; Al-Ajlouni, A. M.; Espenson, J. H. Inorg. Chem. 1996, 35, 1408.
- (a) Gable, K. P.; AbuBaker, A.; Zeintara, K.; Wainwright, A. M. Organometallics 1999, 18, 173; (b) Gable, K. P.; Juliette, J. J. Am. Chem. Soc. 1995, 117, 955.