

H₂-Driven Deoxygenation of Epoxides and Diols to Alkenes Catalyzed by Methyltrioxorhenium

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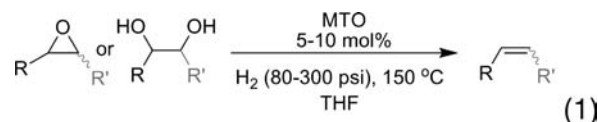
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Catalytic deoxygenation of epoxides and diols is underdeveloped. This reaction is appealing in the context of making value-added organics from biomass. Methyltrioxorhenium (MTO) catalyzes the conversion of epoxides and vicinal diols to olefins with dihydrogen (H₂) as the reductant under reasonably mild conditions (150 °C and 80–300 psi). The only reaction byproduct is water. The reaction is selective for cis cyclic diols, signaling a mechanism of alkene extrusion from a coordinated epoxide via a metallaoxetane intermediate.

Catalytic epoxidation and dihydroxylation of alkenes is a well-studied reaction and widely used in organic synthesis and industry.¹ Its prominence is due, in part, to our reliance on petroleum-based chemicals for the preparation of high-value-added organics (HVOs) that contain heteroatom functionality. In contrast, the reverse reaction, deoxygenation of epoxides and diols to make olefins, is much less developed. Multiple steps and stoichiometric reagents are required.² Only a couple of organometallic oxorhenium complexes have been reported to catalyze the deoxygenation of epoxides to alkenes via oxo transfer to phosphines.³ Cook and Andrews have extended alkene extrusion from [Cp*Re^V(O)(diolate)] to catalytic deoxydehydration of diols with phosphines.⁴ This catalysis is sluggish, limited by requiring slow addition of the excess phosphine to avoid inhibition and overreduction to

rhenium(III), and produces a stoichiometric amount of waste byproduct, phosphine oxide. As society moves toward utilization of biomass and organic renewables for fuels and HVO,⁵ deoxygenation of diols derived from lignocellulosic biomass will become invaluable. Ellman et al. have recently described didehydroxylation of vicinal diols using stoichiometric formic acids at 230–240 °C.⁶ Bullock and co-workers used ruthenium catalysts and dihydrogen (H₂) to convert diols to alcohols under acidic conditions.⁷ In this paper, we report an efficient catalytic method for deoxygenation of epoxides and diols using methyltrioxorhenium (MTO) as the catalyst and molecular hydrogen (H₂) as the reductant, under reasonably mild conditions, 150 °C and 80–300 psi (eq 1).



1-Hexene oxide was initially employed as a prototypical substrate. The addition of 10 mol % MTO to a 1-hexene oxide solution in tetrahydrofuran (THF) in a Parr reactor, which was subsequently pressurized to 300 psi with H₂ and heated to 150 °C, resulted in quantitative conversion of 1-hexene oxide to hexane (96% yield) and a trace amount of 1-hexene (Table 1, entry 1). Reducing the reaction time to 4 h improved the alkene yield to 76%. Nevertheless, significant alkane was still formed (18%) (entry 2). Reducing the pressure to 80 psi elongated the reaction time, as would be expected, but resulted in quantitative conversion to 1-hexene (95%) (Table 1, entry 3).

(5) (a) Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev.* 2006, 106, 4044.
(b) van Haveren, J.; Scott, E. L.; Sanders, J. *Biofuels Bioprod. Biorefining Bioprod.* 2008, 2, 41. (c) See DOE report: Werpy, T.; Petersen, G., Eds. *Top Value Added Chemicals from Biomass*, Vol. 1, 2004, <http://www1.eere.energy.gov/biomass/pdfs/35523.pdf>.

(6) Arceo, E.; Marsden, P.; Bergman, R. G.; Ellman, J. A. *Chem. Commun.* 2009, 3357.

(7) Ghosh, P.; Fagan, P. J.; Marshall, W. J.; Hauptman, E.; Bullock, R. M. *Inorg. Chem.* 2009, 48, 6490.

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







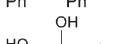

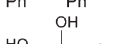





(1) (a) Herrmann, W. A.; Kühn, F. E. *Acc. Chem. Res.* 1997, 30, 169.
(b) Rudolph, J.; Reddy, K. L.; Chiang, J. P.; Sharpless, K. B. *J. Am. Chem. Soc.* 1997, 119, 6189. (c) Jonsson, S. Y.; Fämegårdh, K.; Bäckvall, J.-E. *J. Am. Chem. Soc.* 2001, 123, 1365. (d) Tullo, A. *Chem. Eng. News* 2004, 82, 15.

(2) (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) Larock, R. C. *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*; VCH: New York, 1993; pp 155–156.

(3) (a) Gable, K. P. *Organometallics* 1994, 13, 2486. (b) Zhu, Z.; Espenson, J. H. *J. Mol. Catal. A* 1995, 103, 87. (c) Gable, K. P.; Brown, E. C. *Organometallics* 2000, 19, 944.

(4) Cook, G. K.; Andrews, M. A. *J. Am. Chem. Soc.* 1996, 118, 9448.

Table 1. Deoxygenation of Epoxides and Diols with H₂ Catalyzed by MTO^a

entry	substrate	P _{H₂} / psi	t/ h	major product	% yield ^b
1		300	8		96
2		300	4		76 ^c
3		80	8		95
4		300	0.5		73 ^d
5		300	4		80 ^e
6		300 ^f	8		54 ^g
7		300	8		34 ^h
8		300 ^f	8		50
9		80 ^f	8		18 ⁱ
10		300 ^f	8		60 ^j
11		500 ^k	16		25 ^l

^a Typical reaction conditions: 1.2 mmol of substrate and 0.12 mmol of MTO in THF ($V_{\text{tot}} = 15$ mL) at 150 °C and the specified H₂ pressure in a Parr reactor. ^b Determined by gas chromatography. ^c 18% hexane was formed. ^d The remaining mass balance (ca. 27%) was 1,2-cyclohexanediol. ^e 18% ethylbenzene byproduct. ^f 5 mol % MTO (0.06 mmol) was used. ^g *cis/trans*-stilbene = 2.9; the remaining mass balance was *cis*-stilbene oxide (35%) and its isomerization product *trans*-stilbene oxide (7%). ^h *trans/cis*-stilbene = 4.7; the remaining mass balance was unreacted *trans*-stilbene oxide. ⁱ 3% hexane was also formed. Significant charring was observed under these conditions. ^j In addition, 3% cyclohexane was formed. The remaining balance included unreacted *cis*-1,2-cyclohexanediol (ca. 4%) and its isomerization product *trans*-1,2-cyclohexanediol. ^k 5 mol % MTO at 150 °C in dioxane. ^l In addition, THF (5%) was formed.

The reaction was found applicable to several other epoxides including aromatic and cyclic epoxides (Table 1). Styrene oxide was deoxygenated to styrene with very good selectivity, 80% yield (Table 1, entry 5). Cyclohexene oxide was quite reactive, affording cyclohexene in 73% yield after only 1/2 h reaction time (entry 4). The remaining mass balance was cyclohexanediol. The epoxide in this instant underwent ring opening, which is catalyzed by MTO in the presence of water, a reaction byproduct. *cis*- and *trans*-stilbene oxide afforded moderate yields of both alkene isomers (Table 1, entries 6 and 7), signaling a mechanism that involves isomerization of the epoxide. In the case of *cis*-stilbene oxide, in addition to unreacted *cis*-stilbene oxide (35%), a small amount of *trans*-stilbene oxide (7%) was detected (entry 6).

1,2-Hexanediol exhibited lower activity in comparison to the epoxide and significant charring at 80 psi of H₂ and 150 °C. However, no charring was observed at the higher pressure condition (300 psi), and 1,2-hexanediol converted smoothly to hexane (Table 1, entry 8). In contrast, *cis*-1,2-cyclohexanediol (a cyclic diol) was converted to cyclohexene (60% yield) with a small amount of cyclohexane (3%) as a byproduct (Table 1, entry 10). The reduced yield was due to isomerization of *cis*-1,2-cyclohexanediol to unreactive *trans*-1,2-cyclohexanediol. We observed that the remaining mass balance of the reaction was cyclohexanediol with the isomeric ratio *trans/cis* = 4. In fact, *trans*-1,2-cyclohexanediol did not form any of the corresponding alkene after 8 h at 150 °C and

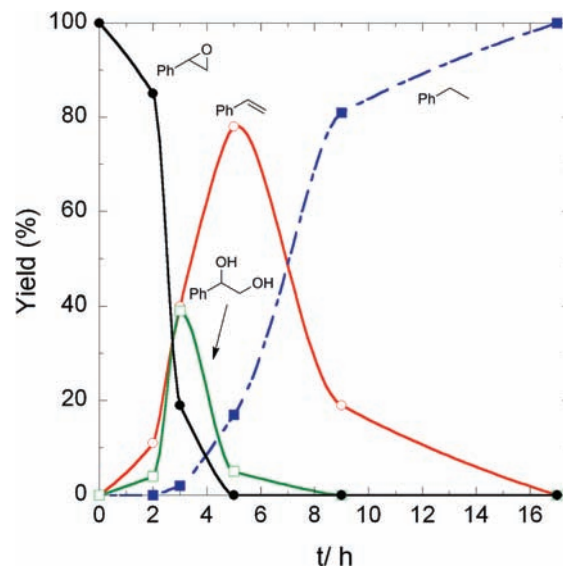


Figure 1. Reaction profile for styrene oxide deoxygenation with H₂ catalyzed by MTO. The lines are an interpolated smoothing function and not a kinetic fit.

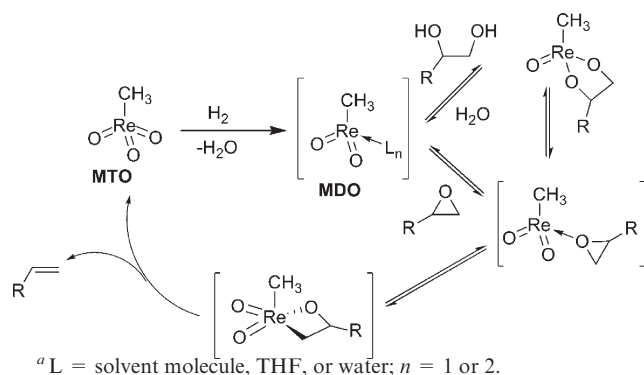
300 psi of H₂ in the presence of 10 mol % MTO. This result is in agreement with a diol deoxygenation mechanism that proceeds through the epoxide. MTO catalyzes the isomerization of the epoxide as observed for *cis*-stilbene oxide and the isomerization of *cis*-1,2-cyclohexanediol to *trans*-1,2-cyclohexanediol via *cis*-cyclohexene oxide. Even though *trans*-1,2-cyclohexanediol may coordinate to rhenium to form a metal diolate, it cannot form a *cis*-epoxide, which requires the intermediacy of the unknown *trans*-cyclohexene oxide, and hence it does not react further.

To investigate the course of the reaction, we collected liquid samples at different time intervals. This required a larger reaction volume (45 mL) to avoid significant depletion from successive sampling. In our experiment, the data from sampling experiments are suitable for semiquantitative analysis and cannot be used to provide precise kinetics. Nevertheless, following the deoxygenation of styrene oxide provided valuable information regarding the sequence of product formation (Figure 1). Early on in the reaction, some styrenediol is formed. MTO is known to catalyze the ring opening of epoxide to diol. Styrene oxide and styrenediol are converted to styrene. The maximum amount of styrene formed is ca. 80% after 4 h, which is quite consistent with that observed for the batch reaction (Table 1, entry 5). Subsequently and after the concentration of the epoxide is depleted, styrene is hydrogenated to ethylbenzene. The use of MTO as an alkene hydrogenation catalyst is new, and the details of this reaction will be reported elsewhere.

To demonstrate the utility of our Diol-to-Alkene Reaction (DARe) in the context of biomass-derived substrates, we investigated the polyalcohol erythritol that is produced from fermentation of starch.⁸ MTO has the advantage of being water-soluble. However, erythritol afforded significant charring under our conditions even at 500 psi of H₂. Nevertheless, erythritol can be converted to 1,4-anhydroerythritol mediated by acid catalysis.⁹ Anhydroerythritol afforded

(8) Kusserow, B.; Schimpf, S.; Claus, P. *Adv. Synth. Catal.* **2003**, *345*, 289.

(9) Childers, K. G.; Dreher, S. D.; Lee, J.; Williams, J. M. *Org. Process Res. Dev.* **2006**, *10*, 934.

Scheme 1. Mechanism Postulated for DARE^a

2,5-dihydrofuran and THF in modest yields (Table 1, entry 11).

The mechanism of epoxide deoxygenation by oxorhenium has been suggested to proceed through a rhenium diolate or an epoxide intermediate that extrudes alkene either via a concerted mechanism or in a stepwise fashion involving a metallaoxetane.^{10,11} Methyl dioxorhenium (MDO) is formed from the reaction of MTO with organic phosphines in organic media and hypophosphorus acid in aqueous solution.¹² We observe under our conditions a change in the color of the catalyst from colorless to red, which is consistent with the formation of MDO.¹³ Upon completion of the reaction, venting of H₂, and exposure of the solution to air, the catalyst reverts to colorless MTO. On the basis of these observations and in conjunction with the stereoselectivity for

cis-1,2-cyclohexanediol and observed epoxide isomerization of *cis*-stilbene oxide, we propose deoxygenation via an epoxide–rhenium adduct (Scheme 1), which extrudes alkene most likely via metallaoxetane, as has been suggested by Gable et al. Kinetic details and their mechanistic implications are in progress.

It is intriguing that an excellent epoxidation catalyst such as MTO^{1a,6,14} can also operate as a reduction catalyst for epoxides and diols. There has been interest in the literature recently on the use of high-valent metal oxo and imido complexes in hydrosilylation reactions.¹⁵ Therefore, future exploration of other metal oxo species in reductions of diols and polyols via the described deoxygenation reaction with molecular hydrogen is a worthwhile endeavor.

In conclusion, we have shown a new catalytic reaction for the deoxygenation of epoxides and vicinal diols to alkenes with molecular hydrogen (H₂) under reasonably mild conditions (150 °C and 5–20 atm). The reaction employs a commercial catalyst (MTO) that is stable to water and air. The featured catalysis is selective and potentially competitive with the standard stoichiometric approaches.² Our results provide evidence for a deoxygenation mechanism that proceeds through a coordinated epoxide and the formation of a metallaoxetane intermediate. The described reaction chemistry is extendable to biomass-derived diols.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(10) Zhu, Z.; Al-Ajlouni, A. M.; Espenson, J. H. *Inorg. Chem.* **1996**, *35*, 1408.

(11) (a) Gable, K. P.; AbuBaker, A.; Zeintara, K.; Wainwright, A. M. *Organometallics* **1999**, *18*, 173. (b) Gable, K. P.; Juliette, J. J. *J. Am. Chem. Soc.* **1995**, *117*, 955.

(12) (a) Felixberger, J. K.; Kuchler, J. G.; Herdtweck, E.; Paciello, R. A.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 946. (b) Abu-Omar, M. M.; Appelman, E. H.; Espenson, J. H. *Inorg. Chem.* **1996**, *35*, 7751.

(13) MTO and H₂ form MDO probably via a [3+2] mechanism. (a) Collman, J. P.; Slaughter, L. M.; Eberspacher, T. S.; Strassner, T.; Brauman, J. I. *Inorg. Chem.* **2001**, *40*, 6272. (b) Dehestani, A.; Lam, W. H.; Hrovat, D. A.; Davidson, E. R.; Borden, W. T.; Mayer, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 3423.

(14) (a) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1638. (b) Espenson, J. H. *Chem. Commun.* **1999**, 479. (c) Owens, G. S.; Arias, J.; Abu-Omar, M. M. *Catal. Today* **2000**, *55*, 317.

(15) (a) Nolin, K. A.; Krumper, J. R.; Pluth, M. D.; Bergman, R. G.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 1468. (b) Du, G.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 5180. (c) Reis, P. M.; Costa, P. J.; Romao, C. C.; Fernandes, J. A.; Calhorda, M. J.; Royo, B. *Dalton Trans.* **2008**, 1727.