Toward Nonoxidative Routes to Oxygenated Organics: Stereospecific Deoxydehydration of Diols and Polyols to Alkenes and Allylic Alcohols Catalyzed by the Metal Oxo Complex $(C_5Me_5)ReO_3$

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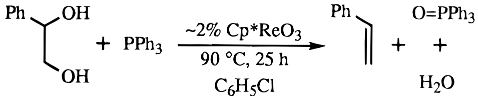
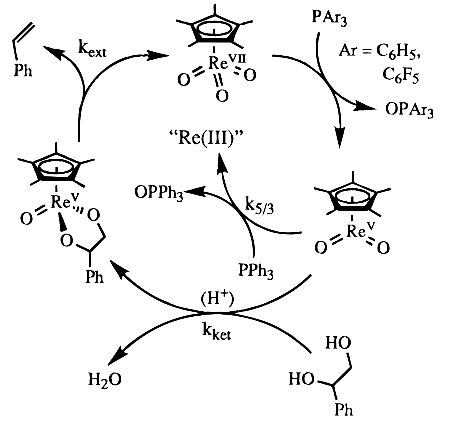
Our research program is exploring *nonoxidative* routes to oxygenated organic compounds starting from renewable biomass carbohydrates.[1,2] Such processes offer significant environmental advantages over conventional approaches based on hydrocarbon oxidation. The latter pose multiple liabilities, ranging from petrochemical extraction and shipping hazards to the coproduction of substantial waste streams due to recalcitrant selectivity problems. Carbohydrates, with one oxygen atom per carbon, are actually too oxygen-rich relative to many important oxygenated organics. Removal of carbohydrate hydroxyl groups would therefore be useful, particularly if a different reactive functional group could be introduced. This has now been accomplished via a new catalytic reaction, the stereospecific deoxydehydration of diols and polyols to alkenes and allylic alcohols. Various stoichiometric reactions effecting the same net transformation, diol didehydroxylation, have already proven valuable in synthetic organic chemistry.[3,4]

Reports of alkene extrusion from metal diolate complexes[5−8] (e.g., Cp*Re(O)(ethanediolate)) inspired us to design a catalytic cycle incorporating this key reaction (Scheme 1, 9−12 o'clock positions). A potential means to complete such a cycle (Scheme 1, 12−3 and 3−9 o'clock positions) was provided by the Cp*Re(O)(diolate) syntheses developed by Gable,[9] employing reactions of diols with an equilibrium mixture[10] of $Cp^*Re^VO_2$ and its dimer $[Cp^*Re^V(O)(\mu\text{-}O)]_2$, prepared in situ by reduction of Cp^*ReO_3.[11,12] Successful implementation of the conceptual catalytic cycle was demonstrated by quantitative conversion of phenyl-1,2-ethanediol ($PedH_2$) into styrene by treatment with triphenylphosphine in the presence of Cp^*ReO_3 in chlorobenzene (55 turnovers/Re; eq 1, Figure 1A).[13,14]



$$\text{PhCH(OH)CH}_2\text{OH} + PPh_3 \xrightarrow[\text{90 °C, 25 h, } C_6H_5Cl]{\sim 2\%\ Cp^*ReO_3} \text{PhCH=CH}_2 + O=PPh_3 + H_2O \qquad (1)$$

Scheme 1. Catalytic Cycle for Diol Deoxydehydration to Alkenes[a]



[a] $Cp^*Re^VO_2$ is in equilibrium with its μ-oxo-bridged dimer $[Cp^*Re^V(O)(\mu\text{-}O)]_2$, either of which may participate in the catalytic cycle.

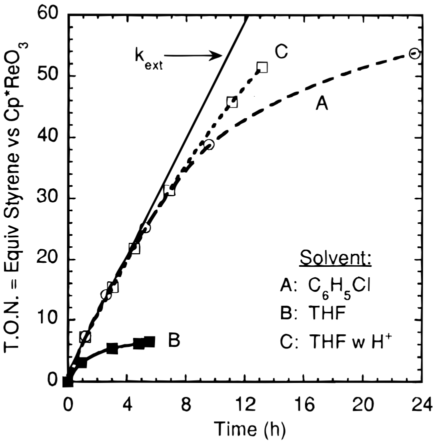


Figure 1. Catalytic reaction profiles for deoxydehydration of phenyl-1,2-ethanediol by PPh_3. [$PPh_3:PedH_2:Re = 68:57:1$, $[Cp^*ReO_3] = 0.65$ mM, $T = 90$ °C.]

Reactions conducted in more coordinating solvents, such as tetrahydrofuran (THF) or *N*-methyl-2-pyrrolidinone (NMP), were much less successful, catalysis ceasing after less than 10 turnovers (Figure 1B). Monitoring of the catalytic reaction in THF-d_8 by ^1H NMR revealed the formation of a new, unidentified Cp*Re-containing species. Stoichiometric control reactions indicate that this results from the instability of $[Cp^*Re^V(O)(\mu\text{-}O)]_2/Cp^*Re^VO_2$ in the presence of excess PPh_3 at 90 °C toward over-reduction to a catalytically inactive Re complex (denoted "Re(III)", Scheme 1, center), as evidenced by formation of the same new Cp* peak observed in the catalytic reactions and roughly 1 equiv of Ph_3PO.[15] Reduction of Re^V to Re^{III} by PPh_3 has precedent in other Re oxo chemistry.[16] While this result explains the probable cause of catalyst deactivation, it does not account for the large solvent effect, since "Re(III)" formation is also observed to occur in benzene-d_6 at a comparable rate ($k_{5/3}$) under stoichiometric conditions ($k_{5/3}(THF)/k_{5/3}(C_6D_6) \approx 2$).

Under catalytic conditions, however, the extent of "Re(III)" formation is a function of the partitioning of the Cp^*Re^V dioxo complex(es) between over-reduction ($k_{5/3}$) and "ketalization" by the diol substrate to yield Cp^*Re^VO(diolate) (k_{ket}, Scheme 1,

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[12] Herrmann, W. A.; Flöel, M.; Kulpe, J.; Felixberger, J. K.; Herdtweck, E. *J. Organomet. Chem.* **1988**, *355*, 297−313.

[13] Standard conditions for $PedH_2$ reactions: $[Cp^*ReO_3] = 0.65$ mM, $PPh_3:PedH_2:Re = 68:57:1$, with PPh_3 added last.

[14] No products from other types of reactions were observed that would correspond to those reported for $MeReO_3$-catalyzed reactions of simple alcohols in the absence of phosphine: Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1996**, *61*, 324−328.

[15] Definitive characterization of this species or its oxidation state has not been undertaken at this point since small amounts of other species are also formed and integration is made difficult by near overlap of some of the Cp* peaks in the ^1H NMR (see Supporting Information).

[16] Conry, R. R.; Mayer, J. M. *Inorg. Chem.* **1990**, *29*, 4862−4867.

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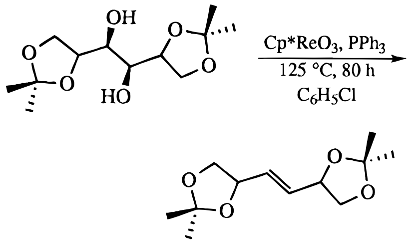
3−9 o'clock positions).[17] This partition ratio was determined experimentally (see Supporting Information): $k_{ket}/k_{5/3} \approx 60$ for benzene-d_6 and $k_{ket}/k_{5/3} \approx 2$ for THF-d_8. The striking solvent dependence is therefore primarily the result of inhibition of diol ketalization by donor/hydrogen-bonding solvents ($k_{ket}(C_6D_6)/k_{ket}(THF) \approx 15$).

The above analysis predicts that catalyst deactivation by "Re(III)" formation can be diminished by either accelerating ketalization or slowing down over-reduction. The former has been accomplished by the addition of *p*-toluenesulfonic acid (pTSA) as a cocatalyst.[9] Reaction of $PedH_2$ under standard conditions[13] in THF in the presence of pTSA (11 equiv/Re) results in 91% conversion to styrene in just over 13 h (Figure 1C). The rate of styrene formation is virtually independent of the decreasing concentrations of both $PedH_2$ and PPh_3 over the course of this reaction, indicating that the rate-limiting step does not depend upon either reactant. This is consistent with extrusion of styrene from Cp*ReO(Ped) being rate limiting, with $k_{ext} = 1.3(1) \times 10^{-3}$ s^{-1} (4.8 turnovers/h) in both THF and NMP in the presence of pTSA at 90 °C. This is in good agreement with the value of 2.1×10^{-3} s^{-1} for styrene extrusion from isolated Cp*ReO(Ped), derived from activation parameters reported by Gable and Juliette.[18]

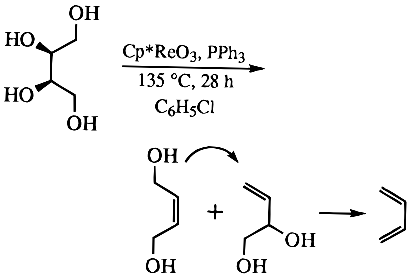
The alternative method of avoiding catalyst deactivation by over-reduction is to decrease $k_{5/3}$. This can be accomplished by utilization of a less active reductant than PPh_3, as demonstrated by deoxydehydration of $PedH_2$ under standard conditions in either benzene or THF using tris(perfluorophenyl)phosphine, $P(C_6F_5)_3$, in place of PPh_3. The rate of product formation in these reactions is identical to that observed in the THF/PPh_3/pTSA system.

The prototype carbohydrate, glycerol, is also cleanly deoxydehydrated by PPh_3 to the corresponding alkene, allyl alcohol (67 turnovers in 23 h), in a biphasic, saturated solution in chlorobenzene at 125 °C without pTSA.[19] The reaction proceeds without significant loss in catalyst activity over the course of the reaction, exhibiting zero-order behavior consistent with an extrusion rate constant from Cp*ReO(glycerolate) of $7.6(4) \times 10^{-4}$ s^{-1} (2.7 turnovers/h). The same reaction conducted homogeneously in NMP in the presence of pTSA (6 equiv/Re) led to gradual catalyst deactivation, allyl alcohol production reaching only 28 of the 68 maximum possible turnovers. The mechanism responsible for catalyst deactivation under these reaction conditions is not yet understood, since changes in the amount of acid- or diol-to-phosphine ratio had little effect and use of $P(C_6F_5)_3$ in place of PPh_3 in the absence of acid gave very few turnovers.

Catalytic deoxydehydration of the protected alditol 1,2:5,6-diisopropylidene-D-mannitol proceeds stereospecifically, as expected,[6,18,20] yielding the corresponding *trans*-alkene (48 turnovers, 86% yield based on diol consumed, eq 2). We have also conducted preliminary studies of unprotected alditols where regiospecificity is a significant consideration. In prior work, we have shown that good to excellent regioselectivity is achievable in the *complexation* of alditols to $(Ph_2PCH_2CH_2CH_2PPh_2)Pt^{II}$ (e.g., 89:11 for 1,2- vs 2,3-coordination of erythritol).[21] Catalytic deoxydehydration of this tetritol under biphasic conditions in chlorobenzene gave the products expected from 1,2- and 2,3-coordination to Re, 3-butene-1,2-diol and *cis*-2-butene-1,4-diol, respectively, in an 85:15 ratio. The major product observed, however, was the fully deoxygenated product butadiene (∼80%, eq 3).



(2)



(3)

This illustrates a limitation inherent in the use of a biphasic carbohydrate/catalyst reaction mixture, presently imposed by catalyst lifetime problems in homogeneous solutions in NMP. The initial deoxydehydration products, in this case the two butenediols, should have much greater solubility in chlorobenzene than the parent polyol; thus multiple, sequential deoxydehydration is favored. Determination of the actual regioselectivity of erythritol deoxydehydration therefore depends on identifying the source of the butadiene. Control experiments show that 3-butene-1,2-diol is readily deoxydehydrated to butadiene by Cp^*ReO_3 in the presence of PPh_3, while there appears to be no direct deoxydehydration of the 1,4-diol isomer. Unfortunately, *cis*-2-butene-1,4-diol is also observed to isomerize to 3-butene-1,2-diol under the catalysis conditions, and therefore it is not possible to determine the true regioselectivity in this system. The major product of xylitol deoxydehydration under similar conditions appears to be 2,4-pentadiene-1-ol.

In summary, the present catalytic method for net didehydroxylation of diols is potentially competitive in many cases with the standard Corey−Winter approach,[22] treatment of the diol thionocarbonate with phosphite reagents at elevated temperatures. Other metal diolate complexes are known to extrude alkene at room temperature;[5,8,23] hence we believe that it should be possible to develop related catalytic cycles for net diol didehydroxylation that function under milder conditions, comparable to the best current stoichiometric methods.[24] Finally, catalytic cycles utilizing more inexpensive, environmentally friendly reductants, such as hydrogen or carbon monoxide, would facilitate bulk carbohydrate deoxydehydration reactions to produce desirable oxygenated organics.

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Supporting Information Available: Full experimental details (7 pages). See any current masthead page for ordering and Internet access instructions.

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[17] This is true regardless of whether over-reduction or ketalization occurs by direct reaction of the μ-oxo dimer $Cp^*_2Re_2O_4$ or via the equilibrium concentration of its monomer Cp^*ReO_2.

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