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Rhenium-Catalyzed Deoxydehydration of Glycols by Sulfite

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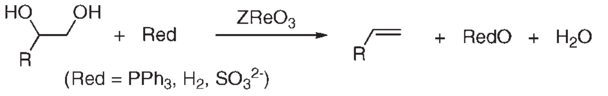
Methyltrioxorhenium and sodium perrhenate catalyze the deoxydehydration of glycols and deoxygenation of epoxides to olefins in moderate yields with sulfite as the reductant.

The drive to develop new and efficient processes for the conversion of abundant renewable resources to chemicals and fuels has spurred new interest in the discovery of selective chemical transformations of biomass-derived carbohydrates and polyols. To access many chemicals and most potential fuels from these resources, partial or complete hydroxyl group removal via dehydration and/or reduction (deoxygenation) is needed.[1] Selective monodehydroxylation of glycols has recently been achieved by hydrogenolysis, catalyzed heterogeneously by Ru−C[2] and homogeneously by Cp*Ru(CO)LH.[3] Reactions that effect both of these changes, i.e., deoxydehydration (DODH, eq 1), are attractive for generating synthetically versatile unsaturated products. Following early studies of stepwise DODH reactions by various reagents,[4] Bergman and co-workers recently reported the efficient high temperature conversion of polyols to olefins by formic acid.[5] The potential of catalyzing DODH reactions by oxo-metal complexes was first demonstrated by Andrews and Cook[6] using PPh_3 as the reductant with Cp^*ReO_3 as the catalyst. Subsequent reports by Gable have shed light on the catalytic pathway of these reactions and have provided more robust rhenium-tris(pyrazolyl)borate catalysts.[7] Most recently, Abu-Omar et al. reported that the deoxygenation of epoxides and DODH of glycols to alkenes and alkanes with the more practical reductant H_2 is catalyzed by $MeReO_3$.[8]



(1)

We have initiated a project seeking the development of new DODH systems that would employ inexpensive reductants and catalysts and the elucidation of their mechanistic pathways. We considered sulfite and bisulfite salts to be attractive reductants for polyol DODH reactions because of their strong reducing potentials,[9] low cost, convenience of use, low toxicity, and recyclability of the byproduct sulfate.[10] Although O-atom transfer reduction of oxo-metal complexes by sulfite/bisulfite is illustrated by the molybdoenzyme sulfite oxidase[11] and model $LMo^{VI}O_2$ complexes,[12] such reactions are rare among other oxo-metal complexes.[13] We disclose here the first examples of catalytic glycol DODH driven by sulfite.

During exploratory experiments, 1-phenyl-1,2-ethanediol (styrenediol) and 1,2-octanediol were tested for reactivity with $NaHSO_3$ and Na_2SO_3 in the presence of selected Mo- and Re-oxo complexes, e.g., $(dedtc)_2MoO_2$, Cp^*ReO_3, and $MeReO_3$ (150−200 °C, organic solvents and biphasic with H_2O).[14] From these experiments, Na_2SO_3 as a reductant and

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(9) ΔG^0 values for the oxo-transfer couple, $X + O \rightarrow XO$, for SO_3^{2-} are −70 to −60 kcal/mol and for HSO_3^- are −60 to −50 kcal/mol, comparable to H_2. (a) Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, *12*, 571. (b) Lee, S. C; Holm, R. H. *Inorg. Chim. Acta* **2008**, *361*, 1166–1176. (c) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401–1449.

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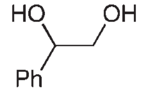
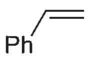
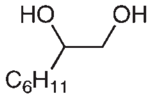
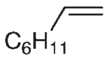
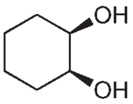
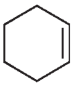
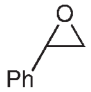
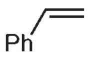
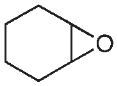
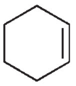
(14) Modest yields (10−30%) of styrene were also produced in some reactions of styrene diol with $NaHSO_3$ or Na_2SO_3 promoted by Cp^*ReO_3, $MeReO_3$, or $(dedtc)_2MoO_2$ at 150−200 °C.

Table 1. Glycol and Epoxide Deoxydehydration by Na_2SO_3/$MeReO_3$ or $NaReO_4$[a]

entry	substrate	catalyst(mol%)	solvent/additive	major product	time (h)	% conv.	% yield[b]
1	 (0.03 M)	$MeReO_3$(10)	benzene		40	90	44
2	(0.2 M)	(8)	benzene		4	100	59
3		(5)	THF		72	25	15
4		(5)	CH_3CN		96	30	15
5		(4)	benzene, $OPPh_3$(10)		48	95	45
6		$MeReO_3$(8)	benzene		168	95	34
7		(8)	PhCl		40	100	45
8		(8)	PhCl, 15-crown-5		21	98	43
9		(2)	none		20	75	60
10		$NaReO_4$(10)	PhCl		88	08	4
11		(10)	PhCl, 15-crown-5		100	100	30
12		(10)	PhCl, 15-crown-5, Na_2SO_4(anhy.)		42	98	38
13		$MeReO_3$(5)	PhCl		48	95	25
14		$MeReO_3$(8)	benzene		30	75	40
15		$MeReO_3$(8)	PhCl		20	95	30

[a] Reactions conducted at 150 °C (oil bath) with 0.2 M glycol or epoxide in the indicated solvent, 1.0−1.5 equiv of Na_2SO_3, and the indicated mol % catalyst. determined by gas chromatography with naphthalene as internal standard with glycol as the limiting reagent [b] Determined by gas chromatography with naphthalene as the internal standard with glycol as the limiting reagent.

$MeReO_3$ as a catalyst appeared most promising and were selected for more thorough study in nonaqueous solvents. Heating a stirred mixture of styrene diol (0.15 mmol), Na_2SO_3 (1.0−1.5 equiv), and $MeReO_3$ (10 mol %) in 5 mL of benzene at 150 °C (sealed tube) resulted in a series of rapid color changes to produce a red brown reaction mixture; GC and GC-MS analysis indicated consumption of the glycol with the formation of styrene in 44% yield and small amounts of dimeric ethers derived from dehydration,[15] possibly promoted by the Lewis acidic $MeReO_3$ (entry 1, Table 1).[16] Increasing the glycol concentration to 0.2 M shortened the reaction time considerably and improved the yield as well (entry 2, Table 1). Since Na_2SO_3 has poor solubility in nonpolar organic solvents, more polar ones, e.g., THF, CH_3CN, and H_2O, were tested in an effort to increase the reaction rate. In the first two solvents, the conversion of styrenediol to styrene proceeded more slowly, perhaps a result of retarding solvent coordination to $MeReO_3$ (entries 3 and 4, Table 1). No appreciable conversion was observed in water. The inclusion of 10 mol % $OPPh_3$, a potential phase transfer catalyst,[17] had minimal effect on the conversion rate (entry 5, Table 1).

Aliphatic diols, such as 1,2-octanediol, better models for carbohydrate-derived polyols, proved less reactive, requiring longer reaction times under comparable conditions in benzene (7 days, entry 6, Table 1) or chlorobenzene (40 h, entry 7, Table 1) to produce moderate yields of 1-octene (no isomers detected by GC/MS), accompanied by small amounts of volatile byproducts (e.g., 2-octanone and dimeric ethers). Seeking to enhance the sulfite solubility and conversion rate, inclusion of 10 mol % of the Na^+-complexing agent 15-crown-5[18] was found to significantly shorten the reaction time (entry 8, Table 1). An initial substrate survey suggests that glycol to olefin DODH by Na_2SO_3/$MeReO_3$ will have a broad scope; e.g., *cis*-1,2-cyclohexanediol was converted to cyclohexene in moderate yield (entry 13, Table 1).[19]

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(15) (a) Gravimetric and NMR/GC-MS analysis of the benzene-soluble material from the styrene diol reaction showed ca. 20−30% by mass of a complex mixture of Ph-containing products, including dimeric ethers (ref 15b); the non-volatile, MeOH-soluble fraction (ca. 10% by mass) appears to be largely $PhCHOHCH_2(OSO_2^-)$ by NMR. (b) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1996**, *61*, 324–8.

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(19) Other glycols producing olefins as major products (unoptimized) include pinacol (2,3-dimethylbutane-2,3-diol) and diethyl tartrate.

Although not yet optimized, practically attractive solventless reactions are also viable. Thus, heating a stirred mixture of 1,2-octanediol (1.2 mmol), Na_2SO_3 (1.5 mmol), and $MeReO_3$ (0.02 mmol) at 150 °C for 20 h in a sealed tube produced a 60% yield of 1-octene at 75% diol conversion (entry 9, Table 1).

Finally, the more economical $NaReO_4$, previously untested for DODH activity, was also found to catalyze sulfite-driven DODH. Heating 1,2-octanediol, Na_2SO_3, and 10 mol % $NaReO_4$ together at 150 °C slowly produced 1-octene with minimal formation of a GC-detectable byproduct; entry 10, Table 1). With this sparingly soluble catalyst and reductant, significant improvements in the conversion rate were achieved by the addition of 10 mol % 15-crown-5 (entry 11, Table 1) and Na_2SO_4 as a dehydrating agent (entry 12, Table 1).

Epoxides are also deoxygenated by the sulfite/$MeReO_3$ system. Styrene oxide and cyclohexene oxide were converted to the corresponding olefins with Na_2SO_3 (1.2 equiv)/$MeReO_3$ (8 mol %) in moderate yield (entries 14 and 15, Table 1) under typical conditions. It is noteworthy that significant quantities of styrene oxide were detected in early stages of the reactions of styrene diol, possibly indicating its intermediacy in DODH. However, the reduction of styrene oxide by Na_2SO_3/$MeReO_3$ under the same conditions as for the glycol reaction (entries 14 and 2, Table 1) actually proceeded considerably slower, 30 h versus 4 h, suggesting that the epoxide is not a primary intermediate in the diol DODH reaction.

Although the mechanistic details of the catalytic cycle are under investigation, existing precedents and our initial observations suggest that two pathways (A and B) are viable, as outlined in Figure 1. In path A, $MeReO_3$ condenses with the glycol to generate Re^{VII}-glycolate **2**; then, **2** is reduced by sulfite to Re^{V}-glycolate **3**. In path B, **1** is first reduced by sulfite; then the resulting $MeReO_2$ (**4**) condenses with the glycol to form glycolate **3**. Finally, fragmentation of **3** produces the olefin with regeneration of $MeReO_3$. The viability of path A is supported by the known reversible condensation of **1** with glycols,[20] which in the case of **1** + styrene diol (1:1, benzene, rt) produced a 3:1 mixture of **1**:**2** (R = Ph). Heating the **1**/**2** mixture or **2** alone (generated from **1** + styrene oxide)[21] with Na_2SO_3 (150 °C, 2−3 h) produced styrene (ca. 50%) and regenerated **1**. The viability of path B is supported by known O-transfer reductions of **1**[22] and our finding that heating **1** with Na_2SO_3 (benzene, 150 °C, 2 h) produces a dark precipitate (presumably a reduced Re species), which, upon the addition of styrene diol to the mixture and continued heating (150 °C, 2 h), also yielded styrene (ca. 60%) and **1**.

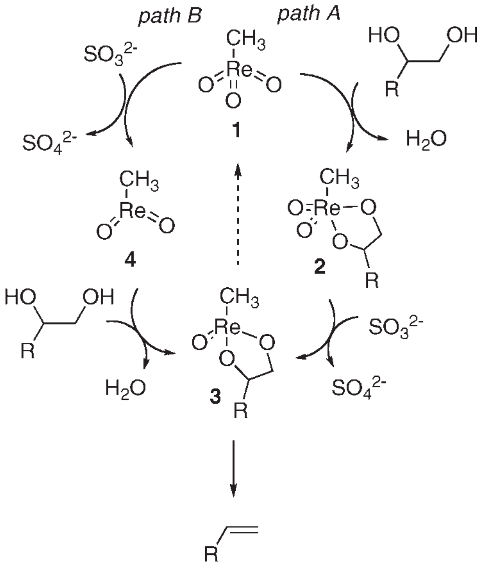

Figure 1. Possible catalytic cycle for sulfite-driven deoxydehydration of glycols.

In conclusion, we have reported here a new method for glycol and epoxide reduction to olefins employing commercial rhenium catalysts and Na_2SO_3 as a reductant that achieves moderate to good efficiency. Studies of the catalytic mechanism and the application of DODH to carbohydrate substrates will be reported in due course.

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Note Added after ASAP Publication. This paper was published on the Web on May 4, 2010, with incorrect values given in reference 9. The corrected version was reposted on May 7, 2010.

Supporting Information Available: Experimental procedures, NMR spectra of reaction mixtures, and representative gas chromatograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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