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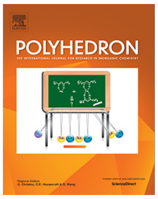

Re-catalyzed deoxydehydration of polyols to olefins using indoline reductants

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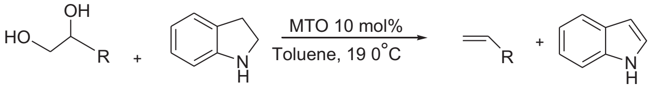
ABSTRACT

A rhenium (CH_3ReO_3, MTO) catalyzed deoxydehyradration (DODH) of glycols to alkenes has been achieved using hydroaromatic compounds as H-transfer reductants. Of the hydroaromatics examined, indoline was the most efficient and proved to be better potential hydrogen donor. The yield of the products is moderate to excellent and the reaction is very clean with the only indole, the oxidized byproduct of indoline detected.



1. Introduction

Declining petroleum resources has made carbohydrates an attractive target for value-added chemicals and renewable energy resources [1]. The conversion of biomass commonly requires the removal of oxygen atoms from the highly oxygenated nature of biomass, which is a critical step to increase the energy content and allow their use as an energy source. Depletion of fossil fuel stocks of energy and their fluctuating costs is a powerful driving force for the discovery and development of proficient methods for the conversion of abundantly available renewable biomass resources to value-added chemicals and fuels. Lately, deoxygenation by reductive processes such as catalytic dehydration, hydrogenolysis, hydrodeoxygenation and deoxydehyadration (DODH) has been well received [2]. In fact, much attention has been focused on DODH (Scheme 1), which effects vicinal OH removal with the formation of olefins [3]. Selective production of value-added chemicals and energy source can be achieved by the deoxygenation of biomass substrate [4]. It produces valuable unsaturated products which are widely used in academia and industry as intermediates and end-products.

The Re-catalyzed DODH reaction of vicinal diols has received increasing attention within the past few years probably because MTO (CH_3ReO_3) is air and water resistant [5]. Oxo-Re catalyzed conversion of diols and epoxides to alkenes was reported by the Abu-Omar group using molecular hydrogen as a reductant [6]. Bergman et al. has employed sacrificial alcohols as a reductant in the presence of $Re_2(CO)_{10}$ [7] Nicholas et al. [8] has applied sulfite as a reducing agent in the presence of various oxorhenium catalysts. The oxo-rhenium catalyzed deoxygenation of epoxides was achieved by Fernandes et al. without a reducing agent [9]. Abu-Omar and Toste's groups independently described rhenium catalyzed DODH and transfer hydrogenation of biomass-derived glycerol, polyols, and sugar alcohols [10,11]. Moreover, Schlaf and Bullock have applied organometallic ruthenium catalysts for the deoxygenation of alcohols [12]. We have also exploited catalysts, $[Cp^*Ru(CO)_2]_2$ for deoxygenation, hydrodeoxygenation and *cis*-$RuCl_2(R_2SO)_4$ for hydrogenolysis of diols and epoxides using hydrogen as a reductant to produce alkanes, alcohols and hydrocracking products [13].

Earlier studies have focused on the development of a catalyst and reductant for the DODH reactions of polyols and epoxides. Among the catalysts, oxo-rhenium compounds such as $MeReO_3$, NH_4ReO_4, Cp^*ReO_3 in combination with various reductants such as triphenyl phosphine [14], molecular hydrogen [6], sulfite [8],

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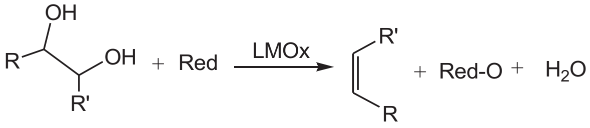


Scheme 1. General Deoxydehydration reaction of glycols.

and Lewis acids (Zn, Fe, Mn, C) [15] have been extensively explored. In addition to oxorhenium compounds, oxo-molybdenum and oxovanadium compounds have also been utilized as DODH catalysts in combination with phosphines and sulfites as reductants. Moreover, sacrificial alcohols as potential H-transfer reductants have also received much attention [7,11,16–18].

In the search for a better hydrogen transfer reductant for metal-catalyzed DODH reactions, we initiated a project for the development of new DODH reaction procedures. The new DODH system must have a practical reductant, which would generate H_2 in situ. Hydroaromatics H-transfer reagents have been used as liquid organic hydrogen carriers for hydrogenation reactions and for hydrogen storage [19]. Various hydroaromatics, are abundantly found in fossil resources. The catalytic activity of redox-active solid metal oxides has been explored for the dehydrogenation of alkyl aromatics [20]. This indicates the potential use of these reductants in homogeneous oxo-metal-catalyzed reactions. Nonetheless, very few hydroaromatics are known for their reactivity with soluble oxo-metal species [21]. Hydroaromatics are visualized as hydrogen carriers and could carry hydrogen safely to the reaction mixture. Sacrificial alcohols including 1-butanol have been used as reductants in the biomass reduction. We report here the MTO catalyzed DODH reactions with a small amount of indoline as reductant and in the absence of 1-butanol (acts as a reducing agent) compared to earlier reports [22], where two reductants, indoline and 1-butanol were used. We revisited the chemistry of $MeReO_3$ and developed a modified process that requires a small amount (3.0×10^{-4} mol) one reductant (indoline) compared to earlier reports. In addition, four different examples (1, 2, 3, 9, 10, Table 1), a comparative study of solvent/catalyst and various catalyst loading compared to ref 22 were studied.

2. Experimental

2.1. General information

All reactants were purchased commercially and used without further purification. All solvents were ACS grade and were used directly. GC–MS analyses were obtained on an Agilent instrument using a Stabilwax capillary column.

Table 1
Optimization.

Entry	Catalyst	Solvent	Styrene (%)	Time (h)
1	NH_4ReO_4	Toluene	67	24
2	Re_2O_7	Toluene	29, 49	2.5, 10
3	$Re_2(CO)_{10}$	Toluene	9	5
4	$MeReO_3$ (MTO) 10 mol%	Toluene	99	2.5
5	MTO, 10 mol%	Benzene	17	2.5
6	MTO, 10 mol%	THF	55	2.5
7	MTO, 10 mol%	Acetonitrile	9	2.5
8	MTO, 10 mol%	Dichloroethane	34	2.5
9	MTO, 10 mol%	Indoline	33	2.5
10	MTO, 10 mol%	Isopropanol	7	24
11	MTO 5 mol%	Toluene	67	2.5
12	MTO 2.5 mol%	Toluene	35	2.5

2.2. Representative procedure for DODH reactions

1-Phenyl-2-ethanediol (0.32 mmol, 44 mg), MTO (0.032 mmol, 8 mg), indoline (0.36 mmol, 34 μL), toluene (1 mL), and dodecane (5 μL) were added to a thick-walled Ace glass tube reactor. The reactor was placed in a heating mantle bath at 190 °C for 2.5 h while stirring magnetically. After cooling to room temperature, the reaction mixture was filtered and analyzed by GC–MS. For NMR of Diprophylline (7-(2,3-Dihydroxypropyl)-3,7-dihydro-1,3-dimethyl-1*H*-purine-2,6-dione), mucic acid (tetrahydroxyadipic acid), and inositol, a 100 μL aliquot of reaction mixture was withdrawn. To this mixture $CDCl_3$ and 2 μL DMSO as internal standard for NMR analysis was added. The product was identified and quantified by ^1H NMR spectroscopy and by comparison with an authentic sample.

2.3. Isolation

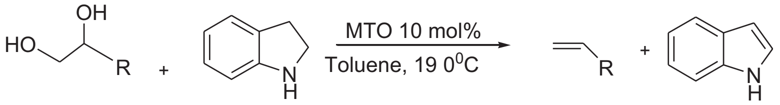
$MeReO_3$ (28 mg, 0.1 mmol), (*R*,*R*)-(+)-hydrobenzoin (214 mg, 1 mmol), indoline (119 μL), and anhydrous toluene (5 mL) were added to a thick-walled Ace glass reactor tube. The reactor was placed in a heating mantle bath in the range of 190 °C for 24 h while stirring magnetically. The reaction mixture 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 (1: 2.5). Product yield was 121 mg, 67%.

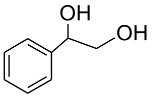
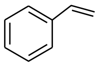
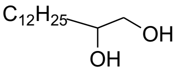
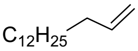
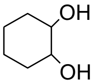
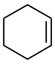
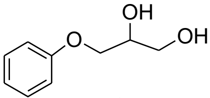
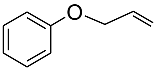
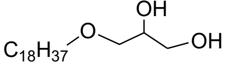
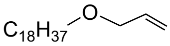
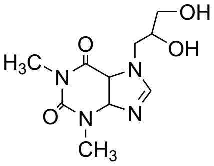
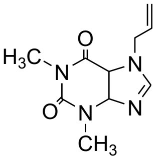
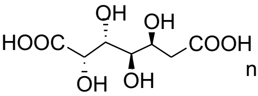
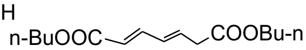
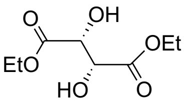
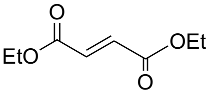
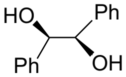
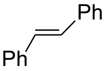
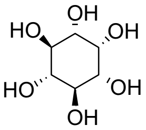
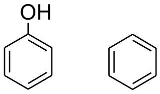
3. Result and discussion

To test the viability of a dihydroaromatic compound as a reductant for the DODH of glycols, an exploratory reaction was carried out with styrene diol, indoline and MTO (10 mol %) in anhydrous toluene, which produced styrene quantitatively in 2.5 h at 190 °C. We began the survey with several Re-catalysts, polar and nonpolar solvents at various temperatures. Among the four-rhenium catalysts examined, MTO was for superior than the others, which produces a quantitative yield of alkene. NH_4ReO_4, Re_2O_7, and $Re_2(CO)_{10}$ also exhibited modest activity and good selectivity to styrene (Table 1, entries 1–4). Catalyst loading is one of the crucial steps in the catalytic cycle. Consequently, to know the efficacy of MTO, we examined MTO loading (10 mol%, 5 mol% and 2.5 mol%) and found that 10 mol% yielded better result of alkene (Table 1, run 4,11,12). The addition of 4 Å molecular sieve did not improve 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 190 °C was the optimum temperature for the model substrate for optimum yield of alkene. We performed the reaction to test the efficacy of hydroaromatic reductants such as 1,2,3,4-tetrahydronaphthalene (tetralin) and indoline under identical reaction conditions. The results demonstrated that indoline proved to be a better hydrogen transfer reagent than 1,2,3,4-tetrahydronaphthalene for DODH of the model substrates. In addition to the excellent yield of olefin produced by indoline, its co-product is indole, which is easily detected by GC. The olefin to indole ratio were found to be close to 1:1.

The results of the conversion of various diols to olefins are shown in Table 2. The olefin formation in the DODH reaction is regioselective since no other isomers were detected. The DODH reaction of styrene diol at 150 °C and 170 °C produced 48% and 58% styrene respectively in 24 h. However, the similar reaction at 190 °C produced a quantitative yield of styrene in 2.5 h (Table 2, entry 1). A long chain glycol, 1,2-tetradecanediol at optimized

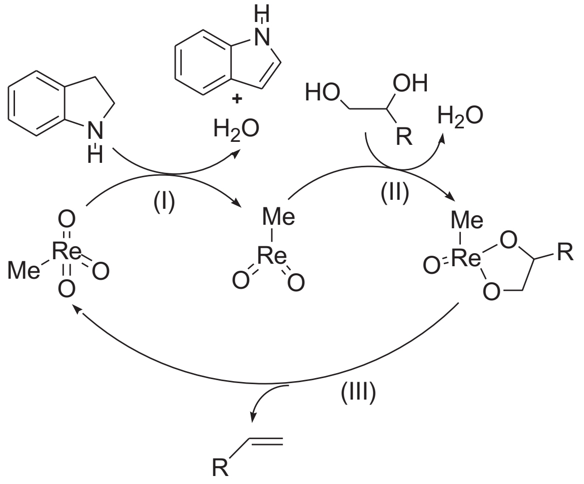
Table 2
Re-Catalyzed DoDH with indoline as reductant.



entry	Glycol	Alkene	T(^{0}C)	Time (h)	Yield (%)$^{a, b}$
1			150 170 190	24 24 2.5	48 58 99 (72)^d
2			190	24	63
3			190	24	9
4			190	5	73
5			190	5, 22	26, 48
6			190	24	70
7			190	48	36$^{c, e}$
8			190	70	58 (41)^d
9			190	24	80 (67)^d
10			190	24	20

^{a}Conversion and yield determined by gas chromatography (GC), with dodecane as the internal standard.
^{b}Isolated yields are given in parentheses.
^{c}Yield determined by ^{1}H NMR.
^{d}^{1}H and ^{13}C NMR of isolated products are given in supplementary materials.
^{e}0.2 M-butenol-1 was added in the reaction.

conditions produced 63% alkene after 24 h (Table 2, entry 2). We found that aromatic diols are more reactive than the aliphatic diols. Furthermore, a cyclic glycol, *cis*-1,2-cyclohexanediol, was very sluggish under these conditions and produced only 9% cyclohexene. However, no reaction with *trans*- cyclohexanediol was detected. This observation implies a *syn* diol elimination, consistent with a concerted fragmentation of the presumed Re-glycolate intermediate. We also examined functional group tolerance of the substrate. Thus, 3-phenoxy-1, 2-propanediol having an ether linkage produced an alkene with a 73% yield in 5 h (Table 2 entry 4). The batyl alcohol (1-*O*-Octadecyl-*rac*-glycerol) that has an ester linkage was slow and produced 26% after 5 h and 48% in 22 h (Table 2, entry 5). Diprophylline (7-(2,3-Dihydroxypropyl)-3,7-dihydro-1,3-dimethyl-1*H*-purine-2,6-dione) produced good yield (70%) of *N*-allyl purine [23]. *N*-Allyl heterocycles, such as *N*-allyl purine (Table 2, entry 6) have wide-ranging biological activity such as drug-induced sleep modulators and spontaneous activity, [24] as selective binders to the A2 adenosine receptor [25] and as anticancer and antiviral agents [26]. The polyhydroxy carboxylic acids, mucic acid (Table 2, entry 7) provided an esterified alkene product,



Scheme 2. Plausible reaction mechanism.

trans, *trans*-diene ester (36%). We also examined the stereoselectivity. The (+) diethyl tartrate is converted steroselectively to diethyl fumarate (58%, Table 2, entry 8) and (*R*, *R*)-(+)-hydrobenzoin to *trans*-stilbene (80%, Table 2, entry 9) at the standard reaction conditions. To diversify the scope and limitation of DODH reaction of biomass-derived polyols, we examined the natural carbohydrate inositol [27]. Benzene and phenol were detected in small quantity. Both these products are quite stable and used industrially in high quantity, which is traditionally produced from petroleum sources. Production of these chemicals from biomass sources would be an advantageous alternative.

In view of these observations and literature precedents a plausible reaction mechanism is shown in Scheme 2. The reaction initiates with reduction of Re(VII) to Re(V) by indoline (I). Consequent formation of rhenium diolate intermediate (II). Olefin extrusion and regeneration of the Re(VII) complete the catalytic cycle (III).

4. Conclusion

In summary, we have revealed for glycol conversion to alkenes using indoline as a potential hydrogen donor and MTO as a pre-catalyst. An attempt will be made for the investigations on elucidating the important catalytic species and mechanisms of these reactions and their application to biomass-derived polyols.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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Supplementary data. Supplementary data

Supplementary data to this article can be found online at 10.1016/j.poly.2018.11.061.

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