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CRITICAL REVIEW
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Rhenium-catalyzed deoxydehydration of renewable triols derived from sugars

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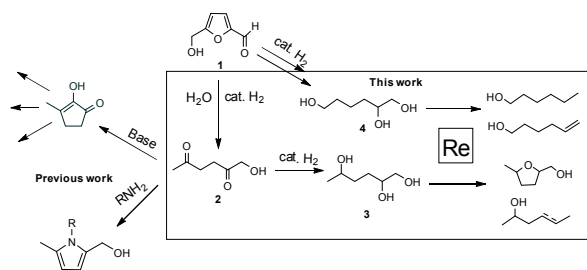
An efficient method for the catalytic deoxydehydration of renewable triols, including those obtained from 5-HMF, is described. The corresponding unsaturated alcohols were obtained in good yields using simple rhenium(VII)oxide under neat conditions and ambient atmosphere at 165 °C.

The dwindling supply of fossil resources as well as the side effects of their continued use, such as global warming, forces us to develop a new and sustainable access to fuels and chemicals.[1] Biomass is the most attractive, globally accessible carbon-rich feedstock that has great potential to replace non-renewable resources.[2] However, biomass-derived raw materials may contain up to 50 wt% of oxygen.[3] Deoxydehydration (DODH) of diols and polyols to the alkenes is one of the most efficient ways to lower the oxygen content of biomass and biomass-derived platform chemicals and could develop into a methodology that allows access to a wide range of valuable chemicals.[4] Several catalysts have been reported to perform this reaction including vanadium[5] and molybdenum[6] complexes. However, rhenium-based catalysts attracted the most attention in the past ten years.[7]

Scheme 1 Synthetic routes for the conversion of HMF (**1**) and HHD (**2**) into useful building blocks

The most common rhenium catalysts used in DODH are MeReO$_3$,[8a], Re$_2$(CO)$_{10}$[8b] and Re$_2$O$_7$ (or HReO$_4$),[8c] however the latter was mainly used as a supported catalyst in heterogeneous systems.[8d] Several reductants have been reported; triphenylphosphine seems to be the most effective, although good results have also been obtained with secondary alcohols. Hydrogen and CO are usually less effective.

Recently, we became interested in the synthesis and applications of 1-hydroxyhexane-2,5-dione (HHD, **2**),[9] which can be obtained in excellent yield by hydrogenation of 5-(hydroxymethyl)furfural (HMF, **1**), a prominent platform chemical derived from carbohydrates (Scheme 1).[10] Herein, we report the homogeneous hydrogenation of **2** to 1,2,5-hexanetriol (1,2,5-HT, **3**), an analogue of 5-HMF-derived 1,2,6-hexanetriol (1,2,6-HT, **4**), which has been reported in the past (Scheme 1, conversion of **2** to **3**).[11] Next, we subjected these biomass-based hexanetriols to DODH using the cheap rhenium catalyst Re$_2$O$_7$ under neat conditions and ambient atmosphere. The generality of this approach was then extended by also investigating various renewable triols e.g butanetriols.[12] Typically, the corresponding alkenes were obtained in very good yields and short reaction times. In addition, a one-pot deoxydehydration-hydrogenation (DODH-HG) approach was investigated, leading to the isolation of 1-hexanol (**13**) from 1,2,6-hexanetriol (**4**).

Results and Discussion

We initiated our studies by examining the hydrogenation of **2** to **3**, which was first described by Descotes' group in 1991.[9a] Recently, a number of studies reported **3** as the by-product,[13] as well as the main product[14] in the hydrogenation of **1** with heterogeneous ruthenium catalysts. However, efficient methods reporting quantitative yields using homogeneous catalysis are absent. We found that use of commercially available Ru-MACHO-BH (cat **I**),[15] a well-known catalyst for a variety of (de)hydrogenation reactions, was quite effective.[16] A near quantitative yield of **3** was achieved after 18 hours at 100°C with 30 bar of H$_2$ using 0.5 mol% of the catalyst and isopropanol as the solvent.
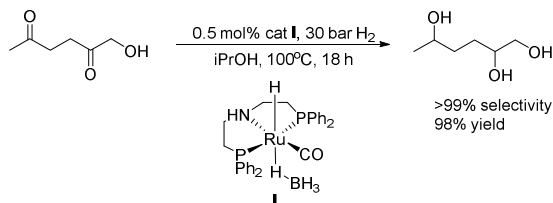
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Scheme 2 Homogeneous hydrogenation of HHD (**2**)

We next examined the DODH of a variety of triols, especially hexanetriols **3** and **4** derived from **1**. Initial reaction optimization was carried out by testing different rhenium sources under aerobic and neat conditions using **4** as a model substrate and triphenylphosphine (PPh$_3$) as a reductant in stoichiometric amounts (Table 1). When 1 mol% of catalyst (respectively 0.5 mol% of dimeric Re$_2$O$_7$) was used, very good yields of 5-hexen-1-ol (**5**) (>95 %) were achieved at full conversion with MeReO$_3$ and Re$_2$O$_7$ (Table 1, entry 1-2). A decrease in activity was found when ammonium- or 2,6-lutidinium[17] perrhenate salts were used as catalysts (Table 1, entry 3,5). On the other hand, no conversion of **4** was observed in the presence of Re$_2$(CO)$_{10}$ under the same experimental conditions (Table 1, entry 4). This may have been caused by its easy sublimation. A decrease of catalyst loading resulted in a decrease in activity, however the DODH still occurs in the presence of 0.1 mol% Re$_2$O$_7$ (Table 1, entry 8). As Re$_2$O$_7$ is more active and remarkably cheaper than MeReO$_3$, it was selected as the rhenium source for further reaction optimization. The combination of Re$_2$O$_7$ and PPh$_3$ has been used before e.g. in deoxygenation of aliphatic epoxides.[18]

Table 1 Catalyst testing in DODH of 1,2,6-HT under aerobic and neat conditions[a]

Entry	Catalyst	Cat loading	Conv.[b] (%)	Yield[b] (%)
1	MeReO$_3$	1 mol%	>99	96 (90)[c]
2	Re$_2$O$_7$	0.5 mol%	>99	98 (91)[c]
3	NH$_4$ReO$_4$	1 mol%	70	67
4	Re$_2$(CO)$_{10}$	1 mol%	-	-
5[d]	(X)ReO$_4$	1 mol%	85	84
6	MeReO$_3$	0.5 mol%	45	43
7	Re$_2$O$_7$	0.25 mol%	79	77
8[e]	Re$_2$O$_7$	0.1 mol%	55	53
9[f]	Re$_2$O$_7$	0.5 mol %	17	15
10[g]	Re$_2$O$_7$	1 mol%	63	13

[a]Reaction conditions: 1,2,6-HT (1.0 mmol), PPh$_3$ (1.1 mmol), catalyst, under air at 165°C, 1 h. [b]Determined by ^{1}H NMR spectroscopy using dimethyl phthalate as an internal standard. [c]Isolated yields, 5 mmol scale. [d]X= 2,6-lutidinium cation [e]6 h. [f]150°C. [g]Without reductant; 34% of 2-THPM was formed

Table 2 Reductant screening in DODH of 1,2,6-HT under neat and air conditions[a]

Entry	Reductant (Eq.)	Conv.[b] (%)	Yield[b] (%)
1	PPh$_3$ (1.1)	>99	98 (91)[c]
2	3-pentanol (2)	42	13
3	3-octanol (2)	>99	51
4	NaH$_2$PO$_2$ (2)	-	-
5	Zn (2)	2	1
6	Na$_2$SO$_3$ (2)	-	-
7	HCO$_2$NH$_4$ (2)	-	-
8[d]	H$_2$	21	5
9[d]	CO	-	-

[a]Reaction conditions: 1,2,6-HT (1.0 mmol), reductant, Re$_2$O$_7$ (0.005 mmol), under air at 165°C, 1 h. [b]Determined by ^{1}H NMR spectroscopy using dimethyl phthalate as internal standard. [c]Isolated yields, 5 mmol scale. [d]7 bar.

Lowering the reaction temperature to 150°C led to a much lower conversion after 1 hour (Table 1, entry 9).

A recyclability test revealed some loss in activity (only 51% yield of **5** under otherwise similar conditions) during the second cycle when 1.1 eq. of PPh$_3$ was used as a reductant (see ESI for details). This loss of activity might be due to excessive rhenium reduction and indeed, the formation of a black, insoluble precipitate suggests the formation of rhenium nanoparticles.[7b,17,19] Working on this premise, we used only 0.95 eq. of PPh$_3$ in the first cycle in order to retain the activity of the catalyst. Reuse of this catalyst with 1.1 eq. of PPh$_3$ in the second cycle lead to the formation of alkene (**5**) in 104% yield (5% of the remaining triol was left after first cycle). It thus appears possible to reuse the catalyst several times.

We have also investigated if 1,2,6-HT **4** could be used as a substrate as well as a reductant hoping to find hex-5-enal as the product. However, the reaction of **4** without PPh$_3$ resulted in cyclic tetrahydro-*2H*-pyran-2-ylmethanol (2-THPM, **14**) as the main product and 13% yield of **5** and no hex-5-enal was obtained (Table 1, entry 10). This result could be expected based on the Lewis acidity of Re$_2$O$_{7.}$ Indeed, the acid-catalyzed synthesis of **14** from **4** has already been reported,[11] and therefore no further studies were carried out on this transformation.
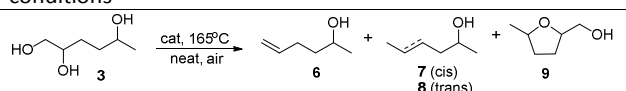
Next, a number of reductants were investigated in order to substitute PPh$_3$ and the results are summarized in Table 2. Unfortunately, only low and moderate yields of **5** were obtained when H$_2$ and secondary alcohols were applied as reducing agents (Table 2, Entry 2-3, 8). Under solvent free conditions, Re$_2$O$_7$ catalyzed DODH with salts as reductants (e.g. sulfites or zinc dust) led to disappointing results. In view of its relatively low price, the excellent yields obtained and the

Journal Name

COMMUNICATION

simple isolation procedure by Kugelrohr distillation (see ESI for details), PPh$_3$ was the obvious choice of reductant.

We have also investigated the influence of oxygen on the process. Notably, a separate experiment under optimized conditions, but under argon atmosphere instead of air gave a 65% yield of **5** (see ESI for details), leading to the suggestion that oxygen plays a role in the catalytic process, which was also observed by Bergman et al.[8b].

Surprisingly, the reaction with 1,2,5-HT (**3**) under the optimized conditions proceeded only to 20% conversion after 1 hour and in addition to 5-hexen-2-ol (**6**) afforded a mixture of *cis-* (**7**) and *trans*-2-hexen-5-ol (**8**). (Table 3, entry 1). Upon increasing the catalyst loading to 3 mol%, complete conversion produced a mixture of **7** (39%) and **8** (25%) as main products. Rhenium-catalyzed isomerization of α-olefin products in DODH

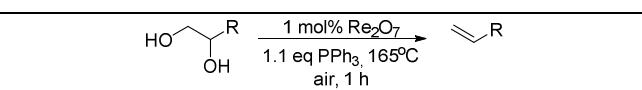**Table 3** Catalytic conversion of 1,2,5-HT under neat and air conditions

Entry	Catalyst (mol %)	Time	Conv^c (%)	Yield^c (%) 6	7	8	9
1^a	Re$_2$O$_7$ (0.5)	1 h	20	10	7	3	-
2^a	Re$_2$O$_7$ (3)	1 h	>99	3	39	25	10
3^{b,d}	Re$_2$O$_7$ (0.5)	10 min	>99				90
4^b	PTSA (0.5)	10 min	51				38
5^b	TFA (0.5)	10 min	-				

^{a}Reaction conditions: 1,2,5-HT (1.0 mmol), PPh$_3$ (1.1 mmol), Re$_2$O$_7$ under air at 165°C. ^{b}Without PPh$_3$ ^{c}Determined by ^{1}H NMR spectroscopy using dimethyl phthalate as internal standard. ^{d}Isolated yield.

was reported before, although the observed amounts of isomers were small.[20] This indicates an interesting OH-position dependence, where isomerization of the double bond occurs dominantly in the case of **3,** yet only marginally for 1,2,6-HT (**4**). When substrate **3** was used as its own reductant, the cyclic product 5-methyltetrahydrofurfuryl alcohol (5-MTHFA, **9**) was obtained with high selectivity (Table 3, entry 3). Various methods exist for the preparation of 5-MTHFA from 5-methylfurfural,[21] however to the best to our knowledge, this is the first report on cyclization of 1,2,5-HT to **9**. Moreover, catalytic amounts of the organic acids TFA (trifluoroacetic acid) and PTSA (p-toluenesulfonic acid) were tested under the same reaction conditions, but only 38% yield of cyclic product **9** at 51% conversion could be detected in the reaction catalyzed by PTSA. Following these results, the substrate scope was investigated by using 1 mol% of Re$_2$O$_7$ in DODH with a variety of triols. In general, the yields and reaction rates were higher with longer alkyl chains in the substrates. Thus, to convert the short-chain triols *i.e.* butanetriols (**10a** and **10b**) and pentanetriols (**10c**), higher catalyst loadings were necessary in order to achieve
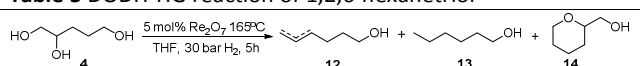
Table 4 DODH of various triols

Entry	Substrate	Product(s)	Conv^b (%)	Yield^b (%)
1	**10a**	**11a**	65	63
2^d			98	97(77)^c
3	**10b**	**11b**	56	28 : 21 **11b:11c**
4^e		**11c**	83	42 : 34 **11b:11c**
5	**10c**	**11d**	92	89
6^f			97	91 (75)^c
7	**10d**	**11e**	>99	98 (90)^c
8	**10e**	**11f**	>99	99 (90)^c

^{a}Reaction conditions: triol (1.0 mmol), PPh$_3$ (1.1 mmol), Re$_2$O$_7$ (0.01 mmol), under air at 165°C, 1 h. ^{b}Determined by ^{1}H NMR spectroscopy using dimethyl phthalate as internal standard. ^{c}Isolated yields, 5mmol scale ^{d}2 mol% Re$_2$O$_7$, 6h, ^{e}5 mol% Re$_2$O$_7$ ^{f}2 mol% Re$_2$O$_7$.

satisfactory results. For example, 1-buten-4-ol (**11a**) was obtained in a good yield using 2 mol% of the catalyst after 6 hours. As expected, when 1,2,3-butanetriol (**10b**) was used as a substrate, the mixture of alkenes **11b** and **11c** was formed. Notably, 5 mol% of Re$_2$O$_7$ was necessary in order to obtain good conversion and yield in 1 hour. On the contrary, the reaction of 1,2,8-octanetriol (**10d**) and 1,2,10-decanetriol (**10e**) with 1 mol% of Re$_2$O$_7$ led to the formation of the corresponding unsaturated alcohols in very good yields. Finally, a one-pot deoxydehydration-hydrogenation (DODH-HG) reaction was tested for the synthesis of saturated alcohols. This transformation has been reported by several groups[22] e.g. for the production of deoxy sugars.[22d] We became interested in the synthesis of 1-hexanol (**13**) from **4**, which could be potentially further converted to 1-hexene,[23] a well-known co-monomer in the production of polyethylene. For this reaction (Table 2, entries 8), THF was used as a solvent and different concentrations of substrate were investigated (Table 5). When high concentrations **4** were used, low yields of **13** were achieved and **14** was formed as the main product (Table 5, entries 1-2). Nevertheless, a mixture of 1-hexen-6-ol and 2-hexen-6-ol was still present after 5 hours. An increase of the yield of **13** was observed at high dilution, but was accompanied by significant charring (Table 5, entry 3). To suppress undesired side reactions, catalytic amounts of supported metals as co-catalysts were used. The best result of 68% yield of 1-hexanol(**13**) at full conversion of the starting

COMMUNICATION

Journal Name

Table 5 DODH-HG reaction of 1,2,6-hexanetriol[a]

Entry	THF (mL)	Co-catal.	Conv. (%)	Yield (%)		
				12	**13**	**14**
1	0.5	-	68	23	9	36
2	2	-	73	19	19	35
3	10	-	>99	-	40	27
4	10	5% Pd/C	>99	-	68(55)[c]	12
5	10	5% Pt/C	>99	-	31	-
6	10	10% Ru/C	>99	-	51	-

[a]Reaction conditions: 1,2,6-hexanetriol (1.0 mmol), Re_2O_7 (0.05 mmol), THF, 30 bar of H_2, 165°C, 5h. [b]Determined by ^1H NMR spectroscopy using dimethyl phthalate as internal standard. [c]Isolated yields, 5 mmol scale.

material was obtained with 0.75 mol% of 5% Pd/C. The product was isolated in 55% yield after flash column chromatography.

Conclusions

In summary, we developed a novel route for the conversion of renewable triols into corresponding unsaturated alcohols. Employing readily available and cheapest rhenium source (Re_2O_7) under neat and ambient conditions at 165°C, we were able to isolate the desired products in good to excellent yields. We have shown that the activity and selectivity of the catalyst depends on the position of a non-vicinal OH group in 5-HMF based hexanetriols. In addition, we performed a one-pot DODH-HG of 1,2,6 hexanetriols resulting in the formation of 1-hexanol. The latter is a potential precursor for 1-hexene, an important co-monomer for poly-ethylene which is currently prepared by trimerisation of ethylene or Fisher-Tropsch on a multi-ton scale. Further investigations on the isomerization mechanism are currently on-going.

Conflicts of interest
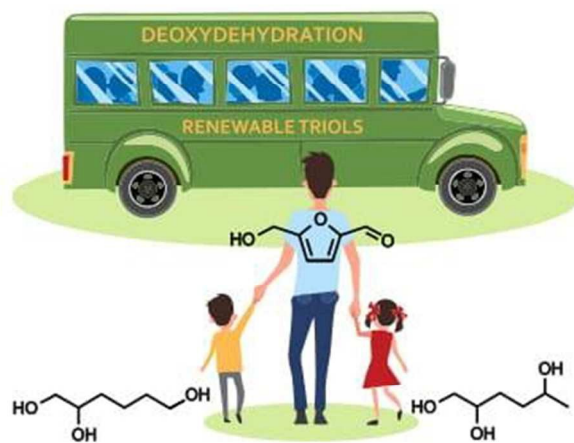
There are no conflicts to declare

Acknowledgments

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