DOI: 10.1002/cssc.201000055

Catalytic Dehydration of Benzylic Alcohols to Styrenes by Rhenium Complexes

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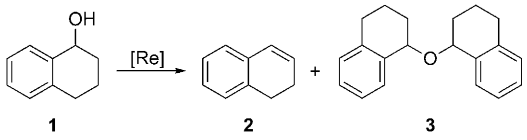
The catalytic dehydration of (poly)alcohols represents a facile route to (functionalized) olefins. Current dehydration methods use strong acids, such as sulfuric acid or *p*-toluenesulfonic acid (*p*TSA),[1] or solid acids, such as zeolites[2] or metal oxides.[3,4] The major problems with these methods are their low selectivity and low functional group tolerance. Therefore a selective, widely useable dehydration method is highly desirable. Such a method might prove useful in the dehydration of biomass-based compounds, which are very rich in hydroxyl groups. Dehydration of both the (hemi)cellulosic components of biomass as well as aromatic lignin components could provide very interesting building blocks for the chemical industry.[5,6]

To date only a few alcohol-to-olefin dehydration reactions catalyzed by homogeneous catalysts have been reported. Catalysts based on ruthenium[7,8] have proven active in the combined dehydration/hydrogenation of diols, and also palladium-[9] and zinc-based[10] catalysts have been reported for the dehydration of alcohols. A remarkable non-metal-based dehydration of glycerol and erythritol that makes use of formic acid was recently reported by Ellman et al.[11]

High-valent rhenium complexes have also shown promising activity in dehydration reactions. Multiple methods were reported: Methyltrioxorhenium(VII) (MTO; CH_3ReO_3) showed good results at room temperature in the dehydration of various alcohols,[12] while in the presence of hydrogen at higher temperature and pressure epoxides were deoxygenated in good and diols in moderate yield.[13] Cp*ReO_3 performed very well in the presence of PPh_3 in the deoxygenation of various diols and polyols,[14] however, phosphine oxide was obtained as a byproduct in quantitative amounts. Herein, we report on a study into various rhenium-based catalysts for the dehydration of alcohols to olefins under mild conditions. We initially focused on the dehydration of various benzylic alcohols.

Following the original procedure by Zhu and Espenson,[12] the first attempts using MTO as a catalyst for the dehydration of 1,2,3,4-tetrahydronaphthol **1** to 1,2-dihydronaphthalene **2** (Scheme 1) at room temperature gave surprisingly poor results. The yield of **2** using benzene as a solvent was only 4%, while 71% was originally reported. In our hands, the highest yield of **2** obtained was 10%, using THF as solvent, a reaction time of 3 days, and 10 mol% MTO as catalyst at room temperature. Using the same procedure at elevated temperature, however, gave very good results. In toluene at 100 °C, complete conversion was obtained after as little as 30 min reaction time, yielding olefin **2** as the single product. Lowering the amount of catalyst to 1 mol% also resulted in complete conversion after 30 min.

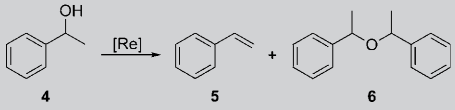


Scheme 1. Rhenium-catalyzed dehydration of 1,2,3,4-tetrahydronaphthol (reaction 1).

Next, different commercially available rhenium complexes were tested for their activity in reaction 1. A blank reaction gave low conversion after 3 days of reaction time, yielding a mixture of both olefin and ether. $Re_2(CO)_{10}$ did show some activity, yet poor selectivity, yielding a 1:1 mixture of olefin and ether after 2 days. Rhenium metal showed a much higher activity as well as selectivity, pushing the reaction to full conversion after 22 h, with good selectivity (87% towards the olefin). The rhenium(VII) complexes MTO, Re_2O_7, and $HReO_4$ performed excellent in this dehydration reaction: all gave full conversion after 1 h and selectively yielded the olefin.

Because excellent results were obtained with reaction 1, the more challenging dehydration reaction of 1-phenylethanol **4** to styrene **5** and the corresponding ether **6** was investigated (reaction 2; Table 1). No reaction was observed in a blank ex-

Table 1. Catalytic activity of rhenium complexes and classic catalysts in the dehydration of 1-phenylethanol **4** to styrene **5** and the corresponding ether **6** (reaction 2).[a]



Catalyst	Amount [mol%]	Conversion[b] [%]	Yield of **5**[b] [%]	Yield of **6**[b] [%]	TOF[c] [h^{-1}]
–	–	0	0	0	0
$Re_2(CO)_{10}$	0.5	92	64	28	13.1
Re metal	1	35	23	16	3.3
$ReCl_3O(PPh_3)_2$	1	17	7	10	0.6
$ReIO_2(PPh_3)_2$	1	>99	81	19	19.1
MTO	1	>99	89	11	36.7
Re_2O_7	0.5	>99	98	1	431
$HReO_4$ (aq)	1	94	56	38	25.5
NBu_4ReO_4	1	0	0	0	0
H_2SO_4	2.5	>99	39	5	52.2
*p*TSA	5	96	85	1	3.4

[a] Reaction conditions: 2 mmol 1-phenylethanol, 0.01–0.1 mmol catalyst, 250 μL pentadecane (internal standard), 10 mL toluene, 100 °C. [b] GC conversion or selectivity after 24 h. [c] Based on the consumption of 1-phenylethanol in the first 30 min

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periment. The use of $Re_2(CO)_{10}$ gave good conversion and selectivity within 24 h of reaction time, while rhenium metal showed poor conversion. For both catalysts, however, the turnover frequency (TOF) was very low. Two rhenium(V) compounds were also tested in this reaction, and while the monooxo species $ReCl_3O(PPh_3)_2$ showed very low conversion, the dioxo species $ReIO_2(PPh_3)_2$ showed full conversion, good selectivity, and a reasonable TOF. Rhenium(VII) compounds also pushed the reaction to completion, while giving good to excellent selectivities towards styrene. MTO and $HReO_4$ showed comparable TOFs in the order of 30 h^{-1}, while Re_2O_7 showed a much higher TOF of 431 h^{-1} and pushed the reaction to completion within only 1 h. The latter TOF is superior to results obtained with both 2.5 mol% sulfuric acid and 5 mol% *p*-toluenesulfonic acid as a catalyst, which showed TOFs of 52.2 and 3.4 h^{-1}, respectively. More interesting is the selectivity of Re_2O_7 compared to the conventional catalysts: Re_2O_7 yielded styrene almost exclusively while sulfuric acid only yielded 39% of styrene, with many styrene dimerization and oligomerization products. Also, *p*-toluenesulfonic acid yielded only 85% of styrene, with the remainder mostly being dimers and oligomers. It can clearly be concluded that in the dehydration of 1-phenylethanol Re_2O_7 outperforms the classical acidic catalysts in both activity and selectivity.

Given these results, the substrate scope of the best-performing catalyst, Re_2O_7, was investigated. Various benzylic alcohols were dehydrated by using 0.5 mol% Re_2O_7, and its performance was compared to 2.5 mol% sulfuric acid as catalyst (Table 2). All secondary and tertiary alcohols were converted completely into the corresponding olefins within 24 h except for cyclohexyl phenylmethanol (entry 6), which showed 91% conversion using the rhenium catalyst. With Re_2O_7, TOFs above 800 h^{-1} were achieved under these conditions. Only the primary non-benzylic alcohol 2-phenylpropan-1-ol (entry 8) did not react with either catalyst. In comparison, it is clear that Re_2O_7 shows superior reaction rates and TOFs for all substrates at lower catalyst loadings, while conversions and selectivities after 24 h are comparable to sulfuric acid.

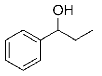
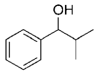
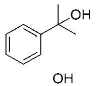
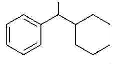
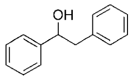
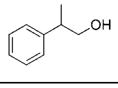
To explore the influence of electronic effects on the dehydration reaction, different *para*-substituted 1-phenylethanol substrates were used in the dehydration reaction catalyzed by either Re_2O_7 or sulfuric acid (Table 3). In both cases a clear correlation between the electron-donating properties of the substituent and the activity in the dehydration reaction was observed: more electron-donating substituents greatly enhance the reaction, while substrates with more electron-withdrawing substituents do not react at all. These observations suggest the involvement of carbenium ions in the reaction mechanism of both catalysts. Further work to explore the reaction mechanism using Re_2O_7 in more detail is ongoing. A comparison of the two catalysts again shows that Re_2O_7 is outperforming sulfuric acid in both activity and selectivity, except when using 1-(4-nitrophenyl)ethanol as substrate. This substrate did not react using Re_2O_7, while it reacted slowly with sulfuric acid.

Table 3. Substituent effect on the dehydration of *para*-substituted 1-phenylethanols catalyzed by 0.5 mol% Re_2O_7 and 2.5 mol% H_2SO_4.[a]

R	Re_2O_7 Conversion[b] [%]	Olefin yield[b] [%]	TOF[c] [h^{-1}]	H_2SO_4 Conversion[b] [%]	Olefin yield[b] [%]	TOF[c] [h^{-1}]
OMe	>99	77	792	>99	11	151
H	>99	97	392	>99[d]	42[d]	52
Cl	>99	67	101	>99	58	28
CN	0	0	0	0	0	0
NO_2	0	0	0	92	42	5

[a] Reaction conditions: 2 mmol *para*-substituted 1-phenylethanol, 0.01 mmol Re_2O_7 or 0.05 mmol H_2SO_4, 250 μL pentadecane (internal standard), 10 mL toluene, 100 °C. [b] GC conversion or yield after 24 h. [c] Based on the consumption of starting material in the first 15 min, average of 2 experiments. [d] After 6 h.

Table 2. Dehydration of various substrates catalyzed by 0.5 mol% Re_2O_7 and 2.5 mol% H_2SO_4.[a]

Entry	Substrate	Re_2O_7 Conversion[b] [%]	Olefin yield [%]	TOF[c] [h^{-1}]	H_2SO_4 Conversion[b] [%]	Olefin yield [%]	TOF[c] [h^{-1}]
1	**1**	>99	>99	>800	>99	>99	154
2	**4**	>99	98	431	>99	39	52
3		>99	>99 (1:13)[d]	464	>99	>99 (1:10)[d]	32
4		>99	>99	54	>99	>99	31
5		>99[e]	90[e]	>800	>99[f]	76[f]	87
6		91	84 (3:1)[g]	164	>99	92 (3:1)[g]	24
7		>99	>99 (1:13)[d]	404	>99	93 (1:11)[d]	13
8		0	0	0	0	0	0

[a] Reaction conditions: 2 mmol substrate, 0.01 mmol Re_2O_7 or 0.05 mmol H_2SO_4, 250 μL pentadecane (internal standard), 10 mL toluene, 100 °C. [b] GC conversion or yield after 24 h. [c] Based on the consumption of starting material in the first 15 min, average of 2 experiments. [d] cis:trans ratio. [e] 15 min reaction time. [f] 1 h reaction time. [g] (Cyclohexylidenemethyl)benzene/(cyclohexenylmethyl)benzene ratio

Interestingly 1-(4-methoxyphenyl)ethanol, which was transformed into the corresponding styrene rapidly and selectively when using Re_2O_7, resembles the *p*-coumaryl alcohol fragment (and other methoxy-substituted phenethyl alcohols) known to be present in softwood lignin and has been used as a lignin model compound in previous research.[15,16]

In conclusion, we have found that rhenium-based catalysts are very effective in the dehydration of benzylic alcohols. Re_2O_7 (0.5 mol%) was shown to perform better in this reaction than the current benchmark catalyst, sulfuric acid (2.5 mol%). In all cases the TOFs of Re_2O_7 were superior to those of sulfuric acid, without sacrificing selectivity for the olefin products. The rhenium-based protocol has shown an excellent activity and selectivity in the dehydration reaction of a methoxy-substituted phenylethyl alcohol and holds great promise for the dehydration of other lignin-based alcohols. This protocol might also be of interest in the field of synthetic organic chemistry for the conversion of readily available benzylic alcohols into styrene moieties. Current research efforts in our laboratory are aimed at broadening the substrate scope of this dehydration reaction towards biomass-based substrates, and at understanding the underlying mechanism.

Experimental Section

General: 1,2-diphenylethanol, 2-methyl-1-phenypropan-1-ol, and cyclohexyl phenylmethanol were synthesized by reduction of the corresponding ketone (Sigma–Aldrich) with 4 equivalents of sodium borohydride (Sigma–Aldrich) in methanol. Sulfuric acid (95–97%) was obtained from Merck and used without further purification. All other compounds were obtained from Sigma–Aldrich or ABCR and used without further purification. GC analysis was performed on a Perkin–Elmer Autosystem XL Gas Chromatograph equiped with an Elite-17 column and a flame ionization detector.

Typical procedure for the rhenium-catalyzed dehydration of alcohols to olefins: Catalyst (0.01 or 0.02 mmol) was dissolved or suspended in toluene (10 mL). Substrate (2 mmol) and pentadecane (250 μL) were added by syringe. The reactor was sealed with a septum and the mixture was heated with magnetic stirring to 100 °C for 24 h. Samples for GC analysis were taken by syringe and filtered over neutral alumina, using acetone as eluent.

Typical procedure for the sulfuric acid-catalyzed dehydration of alcohols to olefins: Substrate (2 mmol) and pentadecane (250 μL) were dissolved in toluene (10 mL). Sulfuric acid (4.9 mg, 2.7 μL, 0.05 mmol) was added by using a Finnpipette. The reactor was sealed with a septum and the mixture was heated with magnetic stirring to 100C for 24 h. Samples for GC analysis were taken by syringe and filtered over neutral alumina, using acetone as eluent.

Acknowledgements

This research was performed within the framework of the CatchBio program. The authors gratefully acknowledge support through the Smart Mix Program of the Netherlands Ministry of Economic Affairs and the Netherlands Ministry of Education, Culture and Science.

Keywords: alcohols · dehydration · elimination · rhenium · styrenes

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Received: February 26, 2010
Revised: March 18, 2010