

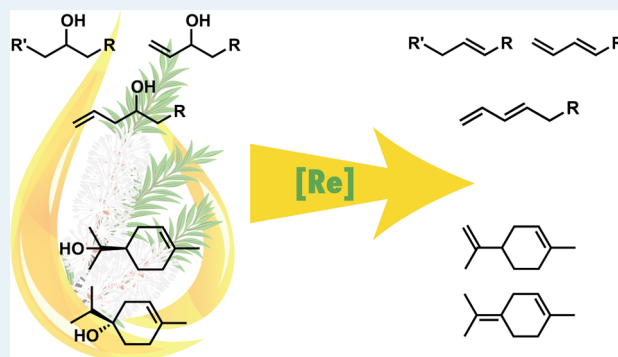
Rhenium-Catalyzed Dehydration of Nonbenzylic and Terpene Alcohols to Olefins

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ABSTRACT: With the increasing importance of research into biomass as a feedstock for the chemical industry, new methods to reduce the oxygen content of biomass are required. Here, we present our progress in the field of the dehydration reaction, using various rhenium-based catalysts, with rhenium(VII) oxide as the most active catalyst. A wide range of allylic, aliphatic, and homoallylic alcohols have been used as substrates under relatively mild conditions (100–150 °C, 0.5 mol % catalyst loading, technical toluene, ambient atmosphere) as well as various biobased terpene alcohols. Furthermore, we have applied our protocol to tea tree oil as a proof of concept for the catalytic upgrading of essential oils. The reactivity and selectivity of rhenium(VII) oxide is compared with a classical acid catalyst; sulfuric acid; and solid acid catalysts, such as acid resins, zeolites, and mesoporous materials. It was found that rhenium(VII) oxide surpasses all these catalysts in both activity and selectivity and also shows enduring activity after seven recycling runs.

KEYWORDS: dehydration, catalysis, rhenium, nonbenzylic alcohols, terpene alcohols



INTRODUCTION

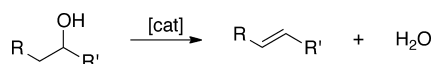
Currently, the majority of the chemical industry is using fossil-based feedstocks. Because these are running out, the search for an alternative resource is of growing importance. A possible alternative resource that could supply the building blocks required by chemical industry in a sustainable fashion is biomass. Biomass can provide sufficient carbon-based material on a yearly basis to supply the current chemical industry with feedstock for production.^{1,2} Biomass, however, is of very different chemical composition from fossil resources. The most important difference is its high oxygen content, which is mostly present in the form of alcohol and ether groups. To obtain building blocks from biomass that are currently used by the chemical industry, this oxygen-to-carbon ratio has to be lowered by either converting or removing the alcohol functional groups.^{3–5} One of the methods to remove alcohol groups is via the dehydration reaction, converting them into olefinic moieties (Scheme 1).

Dehydration reactions are currently performed using strong acid catalysts, such as sulfuric acid or *p*-toluenesulfonic acid,⁶ or solid acids, such as zeolites,⁷ alumina,⁸ or zirconia.^{8,9} The major problems with these methods are their low selectivity and low functional group tolerance as well as their acidic nature, causing reactor corrosion and safety issues. More-selective catalysts for

the dehydration reaction that operate under milder conditions are therefore desirable. We envisage that transition metal-based catalysis can be applied to perform this reaction and meet these criteria.

To date, only a few alcohol-to-olefin dehydration reactions catalyzed by transition metal catalysts have been reported. Zinc-based catalysts have been reported to be active in the dehydration reaction,¹⁰ and catalysts based on ruthenium have been shown to be active in the combined dehydration/hydrogenation of diols.¹¹ An interesting nonmetal-catalyzed deoxydehydration reaction was found in the formic acid-mediated deoxydehydration of polyols.⁹ One of the very promising catalytic systems for the dehydration reaction is based on high-valence rhenium complexes. Methyltrioxorhenium (CH₃ReO₃, MTO) has been found to be active in both the dehydration of alcohols¹² and the deoxydehydration of diols and polyols.^{13–15} Other rhenium(VII) compounds, such as NBu₄ReO₄¹⁴ and Cp*ReO₃ (Cp* = C₅Me₅⁻),¹⁶ have also been found to be active in the deoxydehydration reaction. In addition, the low-valence compounds Re₂(CO)₁₀ and BrRe(CO)₅ have been reported to be active in the deoxydehydration reaction.¹⁴ Recently, we reported on the reactivity of various rhenium complexes in the dehydration of benzylic alcohols to styrenes and found that high-valence rhenium complexes are more active than low-valence rhenium complexes, with

Scheme 1. Dehydration of Alcohols to Olefins

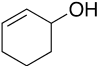

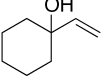
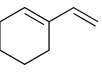
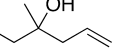
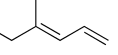
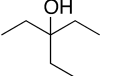
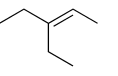
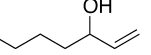
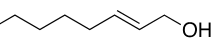


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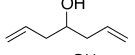
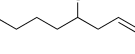
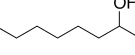

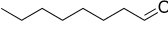
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Table 1. Re_2O_7 - and H_2SO_4 -Catalyzed Dehydration of Tertiary Allylic, Aliphatic, and Homoallylic Alcohols and Secondary Allylic Alcohols^a

Entry	Substrate	Product	Re_2O_7 (0.5 mol%)			H_2SO_4 (2.5 mol%)		
			Time (min)	Yield (%)	Initial rate (mmol h ⁻¹) ^{b,c}	Time (min)	Yield (%)	Initial rate (mmol h ⁻¹) ^{b,c}
1			15	75 ^b	18.5	20	58 ^b	9.35
2			30	56 ^d	12.6	20	80 ^d	10.1
3			60	84 ^{b,e}	1.15	60	60 ^{b,e}	6.29
4			20	96 ^d	4.44	30	95 ^d	4.80
5			5	40 ^{b,f}	8.95	60	29 ^{b,f}	1.0

^aReaction conditions: 2 mmol of substrate, 0.01 mmol of Re_2O_7 or 0.05 mmol of H_2SO_4 , 250 μL of pentadecane (IS for GC) or 0.67 mmol of 1,3,5-trimethoxybenzene (IS for NMR), 10 mL of toluene, air, magnetic stirring, 100 °C, full conversion, all values averaged over 2 runs. ^bBased on GC. ^cRate of consumption of starting material in the first 5 min of reaction. ^dBased on NMR. ^eMixture of isomers, quantified after hydrogenation using 10 wt % Pd on activated carbon. ^f40% conversion.

Table 2. Re_2O_7 - and H_2SO_4 -Catalyzed Dehydration of Primary and Secondary Aliphatic and Homoallylic Alcohols^a

Entry	Substrate	Product	Re_2O_7 (0.5 mol%)			H_2SO_4 (2.5 mol%)		
			Time (h)	Conversion (%) ^b	Yield (%) ^b	Time (h)	Conversion (%) ^b	Yield (%) ^b
1		heptatrienes	4.5	66	33 ^c	24	47	22 ^c
2		octadienes	4	77	38 ^c	4	32	8 ^c
3		1-octene			19			9
		<i>cis</i> -2-octene	3	81	26	24	100	33
		<i>trans</i> -2-octene			29			38
	<i>trans</i> -3-octene			3			21	
4			24	82	18	24	0	0

^aReaction conditions: 2 mmol of substrate, 0.01 mmol of Re_2O_7 or 0.05 mmol of H_2SO_4 , 250 μL of pentadecane (IS), 10 mL of toluene, air (autogenic pressure), mechanical stirring, 150 °C, Parr autoclave, all values averaged over 2 runs. ^bBased on GC. ^cMixture of isomers, quantified after hydrogenation using 10 wt % Pd on activated carbon.

rhenium(VII) oxide (Re_2O_7) as the most active catalyst.¹⁷ With this catalyst, we were able to obtain high yields of styrenes using mild conditions, 100 °C as reaction temperature, ambient atmosphere, and technical grade toluene as the solvent. Furthermore, Re_2O_7 has a higher activity than the benchmark catalyst, sulfuric acid, and displays an increased selectivity to give a higher yield of styrenes.

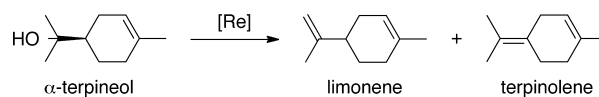
Here, we report on the extension of the scope of the dehydration reaction to nonbenzylic alcohols and terpene alcohols to the corresponding olefins using rhenium(VII) oxide as the catalyst under mild conditions.

RESULTS

First, we set out to explore the reactivity of the Re_2O_7 -based catalytic system to extend the substrate scope beyond benzylic alcohols. A range of allylic, aliphatic, and homoallylic alcohols was tested in the dehydration reaction and compared with the benchmark dehydration catalyst, sulfuric acid (H_2SO_4).

These reactions were performed using technical grade toluene as the solvent under ambient conditions and at a

mild reaction temperature of 100 °C, using 0.5 mol % Re_2O_7 or 2.5 mol % H_2SO_4 . The results are depicted in Table 1. 2-Cyclohexen-1-ol is smoothly dehydrated to cyclohexa-1,3-diene in 75% yield with Re_2O_7 , and H_2SO_4 showed half of the activity of Re_2O_7 and a lower diene yield (entry 1). Substrate conversion is complete, with both catalysts and additional reaction products not mentioned in the table likely being higher-boiling oligomers or Diels–Alder products that do not elute from the GC column. In the dehydration of the tertiary allylic alcohol 1-vinylcyclohexanol, similar catalytic activities were observed, although in this case, H_2SO_4 gives the higher product yield (entry 2). In the case of the tertiary homoallylic alcohol 3-methyl-5-hexen-3-ol, the result is the opposite, with H_2SO_4 being the more active catalyst but Re_2O_7 giving the higher product yield (entry 3). Use of the tertiary aliphatic alcohol 3-ethyl-3-pentanol gave similar activities for both catalysts and also a similar yield (95%) of the corresponding olefin (entry 4). For these tertiary and cyclic secondary allylic alcohols, conversions were complete in only 15 to 60 min of reaction time. When applying the same conditions to the linear

Table 3. Rhenium-Catalyzed Dehydration of α -Terpineol to Limonene and Terpinolene^a

entry	catalyst	time (h)	conversion (%) ^b	yield (%) ^b			initial rate (mmol h ⁻¹) ^{b,d}
				limonene	terpinolene	others ^c	
1		24	0				
2	Re (0)	24	42	28	12	3	0.105
3	Re ₂ (CO) ₁₀ ^e	24	89	62	18	3	0.099
4	Re(CO) ₅ Cl	1.5	>99	50	35	9	1.9
5	ReIO ₂ (PPh ₃) ₂	1.5	>99	61	28	5	2.0
6	ReOCl ₃ (PPh ₃) ₂	3	>99	61	31	2	0.84
7	CH ₃ ReO ₃	4	>99	66	24	3	0.48 ^f
8	HReO ₄ (aq)	1	>99	57	32	6	4.7
9	Re ₂ O ₇ ^e	0.75	>99	65	35		6.3
10	KReO ₄	24	0				
11	NBu ₄ ReO ₄	24	0				
12	NH ₄ ReO ₄	24	12	5	2		<0.1

^aReaction conditions: 2 mmol of α -terpineol, 0.02 mmol of catalyst, 10 mL of toluene, air, magnetic stirring, 100 °C, all values averaged over 2 runs.

^bBased on GC. ^cOther compounds detected: α -terpinene, γ -terpinene, and *p*-cymene. ^dRate of consumption of starting material in the first 15 min (entries 8 and 9), 30 min (entries 4 and 5), 60 min (entry 6), 90 min (entry 7), 4 h (entries 2 and 3), or 24 h (entry 12) of reaction. ^e0.01 mmol of catalyst used. ^fInitiation period of 30 min observed.

Table 4. Effect of Re₂O₇ Loading on the α -Terpineol Dehydration Reaction^a

entry	loading (mol %)	time (h)	conversion (%) ^b	yield (%) ^b			initial rate (mmol h ⁻¹) ^{b,d}
				limonene	terpinolene	others ^c	
1	0.5	0.75	>99	65	35		6.3
2	0.1	5	>99	52	33	8	2.3
3	0.05	4	>99	60	29		1.1
4	0.02	24	89	59	29	1	0.35

^aReaction conditions: 2–50 mmol of α -terpineol, 0.01 mmol of Re₂O₇, 10–250 mL of toluene, air, magnetic stirring, 100 °C, all values averaged over 2 runs. ^bBased on GC. ^cOther compounds detected: α -terpinene, γ -terpinene, and *p*-cymene. ^dRate of consumption of starting material in the first 15 min (entries 1 and 2), 30 min (entry 3), or 120 min (entry 4) of reaction.

secondary allylic alcohol 1-octen-3-ol, complete conversion was not obtained, and no dehydration products were observed; instead, a 1,3-transposition of the alcohol occurred (entry 5). Within 5 min, the reaction with Re₂O₇ reached equilibrium at a 60:40 ratio of the starting compound and 2-octen-1-ol. This is in accordance with an earlier report that gave a similar equilibrium ratio for this 1,3-transposition reaction, catalyzed by MTO.¹⁸ We also found that H₂SO₄ catalyzes this transposition reaction, although not as efficiently as Re₂O₇.

With secondary aliphatic or homoallylic alcohols, no reaction was observed with either catalyst under these reaction conditions. Raising the reaction temperature to 150 °C in an autoclave did allow for the dehydration of these alcohols (Table 2). Using 1,6-heptan-4-ol as the substrate gave a mixture of different heptatrienes. The total yield in heptatriene was determined after hydrogenation to heptane: 35% at 66% conversion for Re₂O₇ after 4 h and 22% at 47% conversion for H₂SO₄ after 24 h (entry 1). Similar results were obtained with 1-octen-4-ol as the substrate and Re₂O₇ as catalyst, yielding 38% of octatriene at 77% conversion of the alcohol, whereas with H₂SO₄, only 8% of dehydration products was obtained at 32% conversion (entry 2).

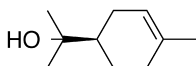
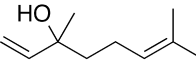
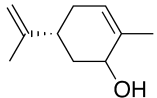
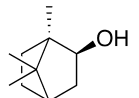
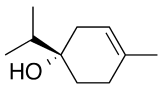
The dehydration of 2-octanol is of particular interest because the corresponding dehydration product, 1-octene, is widely used as a comonomer for polyolefins, such as linear low-density polyethylene (LLDPE).¹⁹ Re₂O₇ gave a good yield of octenes after 4 h (77% yield, 81% conversion), forming a mixture of

primarily 1-, *cis*-2-, and *trans*-2-octene in a 0.75:1:1.12 ratio as determined by GC (entry 3). In the case of H₂SO₄, a similar yield in octenes of 82% was obtained, but after longer reaction time (24 h) and at full conversion. However, with H₂SO₄, much more internal alkenes, including 3-octenes, and only minor amounts of 1-octene were formed. Attempts to dehydrate 1-octanol failed with both catalysts; no reaction was observed with H₂SO₄, while with Re₂O₇, oxidation to octanal was observed together with the formation of trace amounts of octanoic acid and octyl octanoate (entry 4).

When the Re₂O₇-catalyzed reaction with 1-octanol, yielding octanal, was carried out in the absence of air, no conversion was observed, indicating that oxygen from the air serves as the oxidant in this reaction. Oxidative transformations of alcohols to aldehydes and acids using oxygen as oxidant and (supported) rhenium oxides as catalyst are well-known in the literature, although usually higher temperatures are needed.²⁰

Having tested the activity of Re₂O₇ in the dehydration of some typical alcohol structural fragments, we turned our attention to the dehydration of terpene alcohols to terpenes. We first performed a catalyst screening with a series of commercially available rhenium-based compounds in the dehydration of the terpene alcohol α -terpineol using the same reaction conditions, with technical toluene as the solvent under ambient atmosphere and 100 °C as the reaction temperature (Table 3). Under these conditions, the major products in this reaction are limonene and terpinolene, with

Table 5. Re_2O_7 - and H_2SO_4 -catalyzed dehydration of terpene alcohols at 100 °C^a

Entry	Substrate	Products	Re_2O_7 (0.5 mol%)				H_2SO_4 (2.5 mol%)			
			Time (min)	Yield (%) ^b	Selectivity (%) ^b	Initial rate (mmol h ⁻¹) ^b	Time (min)	Yield (%) ^b	Selectivity (%) ^b	Initial rate (mmol h ⁻¹) ^{b,c}
1		limonene	45	>99	65	6.3	45	95	19	6.7
		terpinolene			35				26	
		others ^d			-				50	
2		limonene	45	95	43	18.8	45	84	20	15.0
		terpinolene			22				25	
		2,6-dimethyloctatrienes ^e			32				11	
		others ^f			2				56	
3		<i>p</i> -cymene	30	92	100	>24	30	67	16	13.6
		others ^g			-				84	
4		camphene	15	95	100	9.1	45	97	100	9.7
5		α -terpinene	15	>99	48	8.1	45	82	46	6.7
		γ -terpinene			32				26	
		<i>p</i> -cymene			6				12	
		others ^h			15				17	

^aReaction conditions: 2 mmol of substrate, 0.01 mmol of Re_2O_7 or 0.05 mmol of H_2SO_4 , 250 μL of pentadecane (IS), 10 mL of toluene, air, magnetic stirring, 100 °C, full conversion, all values averaged over 2 runs. ^bBased on GC. ^cRate of consumption of starting material in the first 5 min of reaction. ^d α -Terpinene, γ -terpinene, and *p*-cymene. ^eMixture of isomers, quantified after hydrogenation using 10 wt % Pd on activated carbon. ^f*p*-Cymene and γ -terpinene. ^g*p*-Mentha-2,5,8-triene, *p*, α -dimethylstyrene, and an unidentified product. ^hTerpinolene and isoterpinolene.

minor formation of α -terpinene, γ -terpinene, and *para*-cymene. Most of the tested rhenium-based catalysts showed significant activity in this dehydration reaction. The more active catalysts (entries 4–9) are able to dehydrate α -terpineol with complete conversion within only 4 h of reaction time. The most active catalyst was found to be Re_2O_7 (entry 9), which is able to reach full conversion within only 45 min.

In addition, perrhenic acid (HReO_4 , entry 8), $\text{Re}(\text{CO})_5\text{Cl}$, and $\text{ReO}_2(\text{PPh}_3)_2$ (entries 4 and 5) are very active catalysts, requiring 1 and 1.5 h, respectively, to completely convert α -terpineol to the corresponding terpenes. Concerning selectivity, the best-performing catalyst is again Re_2O_7 . It was the only catalyst that showed only trace formation of side products in this reaction; the other tested rhenium-based catalysts showed 2–9% side product formation.

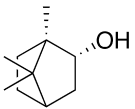
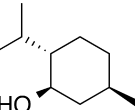
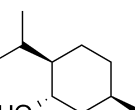
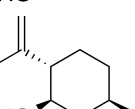
Next, we tested the effect of lowering the amount of Re_2O_7 on the α -terpineol dehydration reaction (Table 4). Using down to 0.05 mol % of Re_2O_7 as catalyst (entries 1–3), full conversion was obtained within several hours, but upon using 0.02 mol % Re_2O_7 , full conversion was not obtained within 24 h (entry 4). The initial rate of the reaction also dropped as a consequence of the lowering of the catalyst amount from 6.3 to 0.35 mmol h⁻¹. Because of these characteristics, we decided to continue using 0.5 mol % of catalyst as the optimal catalyst loading.

After this catalyst screening and loading optimization, Re_2O_7 at 0.5 mol %, as both the most active and selective catalyst, was tested in the dehydration of a broad range of terpene alcohols and compared with sulfuric acid (H_2SO_4) at 2.5 mol % as a benchmark catalyst (Table 5). In the dehydration of α -terpineol (entry 1), H_2SO_4 produces a mixture of five different compounds, with no clear preference for any of the products

and with the highest selectivity for terpinolene at 26%, and Re_2O_7 produced only limonene and terpinolene in a 65:35 ratio. This remarkable selectivity difference was further investigated by testing the reactivity under the reaction conditions of both limonene and terpinolene, which can be considered the primary products of the dehydration of α -terpineol. Using Re_2O_7 , very little isomerization of both compounds (6% and 8% conversion, respectively, after 45 min and an initial rate of 0.16 and 0.10 mmol h⁻¹) is observed, whereas with H_2SO_4 , rapid reaction toward α -terpinene, *p*-cymene, and γ -terpinene is observed (33% and 22% conversion, respectively, after 45 min and an initial rate of 1.0 and 0.58 mmol h⁻¹). In the dehydration of (-)-linalool (entry 2), similar results were obtained, with Re_2O_7 showing somewhat better activity, but a much better selectivity. With Re_2O_7 , three products are formed in significant amounts, with limonene as the major product in 41% selectivity, and with H_2SO_4 , six products are formed with terpinolene as the major product in only 25% selectivity.

The formation of limonene and terpinolene from linalool is a known reaction and has been proposed to proceed via an allylic carbocation intermediate, which shifts from the 3- to the 1-position, followed by ring closure and deprotonation.¹⁹ In the case of carveol, the difference in both selectivity and activity is even larger: with Re_2O_7 , *para*-cymene is formed as the only product in a very good yield of 92%, whereas with H_2SO_4 , multiple compounds are formed, and only 16% selectivity for *para*-cymene is obtained (entry 3). On the other hand, when using isoborneol as substrate, not much difference is observed between the two catalysts, both forming exclusively camphene via the well-known Wagner–Meerwein rearrangement (entry 4).²¹ Also in the case of (-)-terpinen-4-ol, little difference is

Table 6. Re_2O_7 - and H_2SO_4 -Catalyzed Dehydration of Terpene Alcohols at 150 °C^a

Entry	Substrate	Product	Time (h)	Re_2O_7 (0.5 mol%)			H_2SO_4 (2.5 mol%)			
				Conversion (%) ^b	Yield (%) ^b	Selectivity (%) ^b	Time (h)	Conversion (%) ^b	Yield (%) ^b	Selectivity (%)
1		camphene	48	51	51	51	48	56	42	100
		camphor				49				-
2		<i>p</i> -menth-1-ene ^c	24	>99	>99	11	48	12	12	-
		<i>p</i> -menth-2-ene ^c				82				93
		<i>p</i> -menth-3-ene ^c				7				7
3		<i>p</i> -menth-1-ene ^c	24	>99	>99	6	48	57	54	1
		<i>p</i> -menth-2-ene ^c				85				90
		<i>p</i> -menth-3-ene ^c				9				9
4		α -terpinene	24	79	16	32	24	30	4	- ^e
		isoterpinolene				42				- ^e
		others ^d				26				- ^e

^aReaction conditions: 2 mmol of substrate, 0.01 mmol of Re_2O_7 or 0.05 mmol of H_2SO_4 , 250 μL of pentadecane (IS), 10 mL of toluene, air (autogenic pressure), magnetic stirring, 150 °C, Ace pressure tube, all values averaged over 2 runs. ^bBased on GC. ^c*p*-Menth-1-ene, 4-isopropyl-1-methylcyclohexene; *p*-menth-2-ene, 3-isopropyl-6-methylcyclohexene; *p*-menth-3-ene, 1-isopropyl-4-methylcyclohexene. ^dPulegol, γ -terpinene, and *p*-cymene. ^eTrace amounts of α -terpinene and *p*-cymene together with pulegol.

observed in activity and selectivity, although a higher total yield is obtained in a shorter time when using Re_2O_7 as the catalyst (entry 5).

All terpene alcohols mentioned in Table 5 were dehydrated at a reaction temperature of 100 °C. Interestingly, the reaction of (–)-borneol, the stereoisomer of isoborneol, did not proceed with either catalyst at this temperature. When the reaction temperature was raised to 150 °C, however, both Re_2O_7 and H_2SO_4 convert borneol to camphene in 51 and 56% conversion, respectively, although in the case of Re_2O_7 , oxidation to camphor was also observed (Table 6, entry 1).

In addition, the secondary aliphatic alcohols menthol and isomenthol (entries 2 and 3) did not react at 100 °C, but were converted smoothly at 150 °C to the corresponding menthens with Re_2O_7 , whereas H_2SO_4 showed moderate to poor conversions, even after 48 h. The secondary homoallylic alcohol isopulegol (entry 4) gave a poor mass balance with both catalysts at 150 °C, indicating the formation of side products with higher boiling points.

Because we demonstrated the use of Re_2O_7 as a potent catalyst for the dehydration of various terpene alcohols to terpenes, we decided to apply this procedure to tea tree oil as a proof of principle for the catalytic upgrading of essential oils. Tea tree oil is the essential oil obtained by pressing the leaves of the *Melaleuca alternifolia* and consists mostly of terpinen-4-ol (48%, Table 7) and α - and γ -terpinene (10% and 23%, respectively), with minor amounts of α -terpineol (7%) and some other terpenes. We applied our Re_2O_7 -catalyzed dehydration protocol on this essential oil and were able to upgrade the oil within 30 min, converting all terpene alcohols and yielding 35% and 39% of α - and γ -terpinene, respectively, as the predominant compounds. Because the dehydration products are already present in the untreated oil, the upgraded oil contains fewer components, thus increasing both yield and ease of separation of the terpenes. With H_2SO_4 , a similar

Table 7. Re_2O_7 - and H_2SO_4 -Catalyzed Dehydrative Upgrading of Tea Tree Oil^a

compound	tea tree oil	Re_2O_7 (0.5 mol %, 30 min)	H_2SO_4 (2.5 mol %, 3 h)
terpinen-4-ol	48	0	0
α -terpineol	7	0	0
α -terpinene	10	35	34
γ -terpinene	23	39	36
limonene	1	5	4
terpinolene	4	9	13
isoterpinolene	0	2	0
<i>p</i> -cymene	7	11	13
mass balance		92	86

^aReaction conditions: 617 μL of tea tree oil, 0.01 mmol of Re_2O_7 or 0.05 mmol of H_2SO_4 , 250 μL of pentadecane (IS), 10 mL of toluene, 100 °C, air, magnetic stirring, 30' or 3 h, values are selectivities based on GC and averaged over 2 runs.

mixture was obtained after the reaction, but it took 3 h to completely convert all the terpene alcohols to terpenes.

During all experiments performed with Re_2O_7 as the catalyst, it was observed that Re_2O_7 does not (completely) dissolve in the reaction medium and is seemingly acting as a heterogeneous catalyst. We therefore have also compared Re_2O_7 with various commonly used solid acid catalysts. In Table 8, the results of the dehydration of α -terpineol using various commonly used solid acid catalysts are given, again using technical toluene as the solvent under ambient atmosphere and 100 °C as the reaction temperature for all catalysts. γ -Alumina (entry 3) showed no reactivity in this reaction, and also the Brønsted acidic resins Amberlite IR120 and Dowex 50WX8 (entries 4 and 5), both styrene divinylbenzene polymers functionalized with sulfonic acid groups, showed no or very little reactivity in this reaction under the given reaction conditions. Montmorillonite K10 (entry 6), a Brønsted acidic clay, showed reasonable activity in this reaction, although the

Table 8. Dehydration of α -Terpineol Using Various Acid Catalysts^a

entry	catalyst	conversion (%) ^b	yield (%) ^b					initial rate (mmol h ⁻¹) ^{b,c}
			limonene	terpinolene	α -terpinene	p-cymene	other	
1	Re ₂ O ₇ ^d	>99	65	35				6.3
2	H ₂ SO ₄ ^{d,e}	>99	24	24	24	13	11	6.7
3	γ -Al ₂ O ₃	0						
4	Amberlite IR120	5	1	1				<0.01
5	Dowex 50WX8	0						
6	Montmorillonite K10	86	14	18	9	14	6	1.2
7	H-ZSM-5	12	3	3				0.01
8	H-Beta	59	22	12	3	8	4	0.49
9	H-Y	69	18	12	2	15	5	1.8
10	Al-MCM-41	51	16	15	3	6	6	0.05

^aReaction conditions: 2 mmol of α -terpineol, 4.8 mg of catalyst, 10 mL of toluene, 100 °C, air, magnetic stirring, 24 h, all values averaged over 2 runs. ^bBased on GC. ^cRate of consumption of starting material in the first 15 min (entries 1, 2 and 6) or 30 min (entries 8 and 9) of reaction. ^d30 min reaction time. ^e0.05 mmol catalyst used.

selectivity was roughly comparable to that of sulfuric acid and, thus, much lower than Re₂O₇.

Next, three different zeolites were tested, ranging from medium- to large-pore-size zeolites. ZSM-5 showed a low activity under these reaction conditions (entry 7), whereas zeolites Beta and Y showed much higher activity, with the latter being the more active (entries 8 and 9). In addition, the mesoporous aluminosilicate Al-MCM-41 showed activity in this reaction (entry 10). All these solid catalysts showed similar selectivities, giving a mixture of five different compounds. Re₂O₇ is the one exception, showing a high reaction rate in combination with the formation of only two reaction products in quantitative yield.

Another important characteristic of a solid catalyst is its recycling behavior. Recycling tests for Re₂O₇ were performed on the dehydration of α -terpineol. Recycling was carried out by centrifugation of the reaction mixture after the catalytic run and subsequent decantation of the solution, followed by addition of a new substrate solution. Seven subsequent runs were carried out in this manner, and both the product yield after 45 min and the initial reaction rate were recorded (Figure 1). It was found that full conversion was reached after 45 min during three consecutive runs, but that activity was gradually lost during the seven runs performed. Despite this activity loss, Re₂O₇ still showed an activity of 1.1 mmol h⁻¹ in the seventh run, which is comparable to other solid catalysts in their first run, as described above. The selectivity of Re₂O₇ remained unchanged

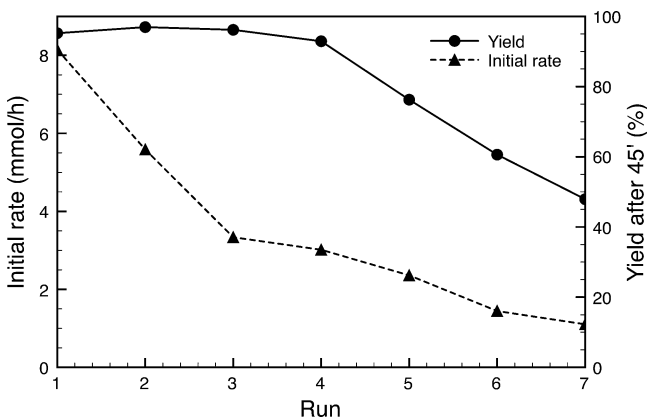


Figure 1. Recycling characteristics of the Re₂O₇-catalyzed dehydration of α -terpineol.

during all runs, with limonene and terpinolene as the major products and only trace formation of other products observed.

One of the factors involved in the recyclability of Re₂O₇ is its (partial) solubility in the reaction medium. This factor was monitored by filtration over Celite of a reaction mixture after a catalytic run and subsequent addition of a new substrate solution. The initial rate in the filtrate was compared with a run that was not filtered. Although the observed initial rate in the filtrate was much lower than that of the nonfiltered reaction mixture (1.4 versus 5.2 mmol h⁻¹ respectively), the activity that was found for the filtrate was considerable. This also indicates that both dissolved (homogeneous) and solid (heterogeneous) Re₂O₇ exhibit catalytic behavior.

DISCUSSION

Rhenium-Based Catalyst Activity. In the dehydration of benzylic alcohols with rhenium-based catalysts, we previously described a trend of increasing reactivity (based on the initial rate of reaction) with increasing oxidation state of the rhenium metal.¹⁷ The same trend in reactivity was observed in the catalyst screening for the dehydration of α -terpineol, with Re metal and Re₂(CO)₁₀ showing low activity, the Re(V) species showing good conversion at intermediate activity, and Re₂O₇ and HReO₄ being the best performing catalysts in terms of both conversion and activity. The only catalyst that falls outside of this trend is Re(CO)₅Cl, which shows activity similar to the Re(V) species. Also remarkable is the relatively low activity of MTO in comparison with the other catalysts tested in this study and also in comparison with previously obtained results. With this catalyst, we observed an initiation period of 30 min, indicating the formation of an active species other than MTO itself. Further research would be required to determine the nature of this species. Another interesting observation is the very low or even complete lack of activity of the perrhenate salts.

One of the factors that could be considered to explain the observed trends in reactivity for these rhenium-based complexes is their Lewis acidic strength. A higher oxidation state implies a higher Lewis acidic strength, which would enhance binding to the electron-rich alcohol group, thereby weakening the C–O bond and activating the substrate for dehydration, thus giving higher activity. The lack of reactivity of the perrhenate salts can also be explained in terms of Lewis acidic strength: because these perrhenates are negatively charged, they are Lewis bases and will therefore be reluctant

to bind with the electron-rich alcohol group. The ligands attached to the rhenium center exert an additional influence on the Lewis acidic strength of the complexes. Oxo and halide ligands are both σ and π electron donors, which lowers the Lewis acidic strength of the rhenium center, whereas carbonyl ligands being π acceptors will attenuate the Lewis acidity of the rhenium center and, accordingly, may have an activating effect on the complex. This could explain the relatively high activity of $\text{Re}(\text{CO})_5\text{Cl}$, even though this is a $\text{Re}(\text{I})$ species and cannot be considered a Lewis acid.

Another factor of influence on the overall reactivity is the steric demand around the metal center, which is dependent on the number and size of the various ligands. In the case of $\text{ReO}_2(\text{PPh}_3)_2$ and $\text{ReOCl}_3(\text{PPh}_3)_2$, the triphenylphosphine ligands might cause considerable steric hindrance around the metal center, hampering the binding of the alcohol and, thus, lowering the overall activity. Furthermore, these complexes show very different solubility characteristics, which might also play a role. Finally, the oxidation state of the complexes also may change under reaction conditions, making the exact active species unknown at this point: the low-valence rhenium complexes could be oxidized to high-valence species because the reactions are performed in air. However, we do not observe any increase in activity during the reaction when using low-valence rhenium compounds. We also do not observe a significant color change during the reaction, and rhenium complexes in higher oxidation state are usually clearly colored. Only after prolonged reaction time color changes are observed. This indicates that any potential oxidation is a slow process compared with the rate of the dehydration reaction, thus having a minor influence on the dehydration reaction.

Because the presence of air is required for the reaction to proceed, it is possible that oxygen is involved in the reaction. Possibly the rhenium-catalyst is reduced during the catalytic cycle and requires oxidation for the catalysis to occur. For MTO, it is known that it can be reduced by PPh_3 ,²² sulfite,¹⁵ or H_2 ¹³ to form a rhenium(V) species and also an alcohol can reduce the rhenium, yielding the corresponding ketone.²³ However, except for the reactions with 1-octanol and borneol, performed at higher temperatures and with an alcohol difficult to dehydrate, we do not detect any traces of ketone at any point in the dehydration reaction of all other alcohols tested, rendering this pathway unlikely.

Furthermore, the presence of water could play a role; for instance, in the case of Re_2O_7 , which is known to react with water to form perhenic acid (HReO_4). The considerable difference in initial rate between these two catalysts (4.7 vs 6.3 mmol h^{-1}) indicates that the activity observed for Re_2O_7 at the start of the reaction can be ascribed to Re_2O_7 itself. As the reaction progresses however, the formation of HReO_4 cannot be excluded as a contributing factor to the overall activity.

In conclusion, many factors are at play in determining the overall reactivity of these rhenium-based dehydration catalysts. Mechanistic studies are currently carried out on the rhenium-mediated dehydration reaction, which are expected to provide further insight into this matter.²¹

Nonbenzylic Substrate Reactivity. In the dehydration of nonbenzylic alcohols, two different trends in reactivity can be observed. When comparing the different tertiary alcohols tested (entries 2–4 in Table 1), the initial rate decreases from the allylic to the aliphatic to the homoallylic tertiary alcohol. Also when comparing the secondary alcohols tested (entry 2, table 1 and entries 1–3, table 2), it is observed that the allylic

secondary alcohol does react at 100 °C, but the aliphatic and homoallylic secondary alcohols do not. Furthermore, the aliphatic secondary alcohol 2-octanol shows a higher conversion in a shorter reaction time than the homoallylic alcohols. Overall this leads to the following trend in substrate reactivity:

allylic > aliphatic > homoallylic alcohols

When comparing the various aliphatic alcohols (entry 4, Table 1 and entries 3 and 4, Table 2), it is observed that the tertiary alcohol reacts at 100 °C, the secondary only at 150 °C, and the primary alcohol does not show any dehydration reaction at 150 °C. Also upon comparing the homoallylic alcohols (entry 3, Table 1 and entries 1 and 2, Table 2), it is observed that the tertiary homoallylic alcohol reacts at 100 °C, but the secondary homoallylic alcohols only react at 150 °C. This thus points to the following trend in substrate reactivity:

tertiary > secondary >> primary alcohols

Both these trends follow the trend in carbocation stability, indicating that a carbocation intermediate could be involved in the rhenium-catalyzed dehydration reaction. The acid-catalyzed dehydration of alcohols is known to proceed via a carbocation intermediate.^{24,25} Combined with the observation that the rhenium-catalyzed and acid-catalyzed dehydration reactions show much similarity in terms of reactive substrates and formed products, it is likely that the rhenium-catalyzed dehydration reaction also proceeds via a carbocation intermediate; however, it seems that the mere involvement of a carbocation intermediate is not the only product-determining factor. Although we see mostly the same products formed with both types of catalyst (rhenium and acid), the difference in selectivity between the two in various dehydration reactions, such as the dehydration of α -terpineol or linalool, is too large to conclude that the same mechanism is in operation. More studies are currently in progress to elucidate the mechanism of the rhenium-catalyzed dehydration reaction.

Terpene Alcohol Reactivity. When considering the results of the various tested terpene alcohols with both Re_2O_7 and H_2SO_4 , it becomes clear that in most cases, Re_2O_7 shows activity similar to or higher than H_2SO_4 . Of equal importance is the product selectivity, which is at least as high and in some cases much higher with Re_2O_7 . With several substrates, such as α -terpineol, carveol, and linalool, the selectivity for a single product is much higher than with H_2SO_4 , whereas with substrates such as terpinen-4-ol and (iso)menthol, the selectivity is similar, but the total yield of products is significantly higher with Re_2O_7 than with H_2SO_4 . The very high selectivity of Re_2O_7 in the dehydration of α -terpineol can be attributed to the 6-fold lower rate of isomerization of the primary products limonene and terpinolene in comparison with H_2SO_4 , whereas the rate of the dehydration reaction is comparable for both catalysts.

In the reactivity of the tested terpene alcohols, an interesting difference is observed between isoborneol and its isomer borneol. The former is dehydrated at 100 °C, and the latter needs 150 °C to be dehydrated to camphene. To explain this difference in reactivity, two factors can be involved. The first is the electronic nature of the C–O bond, in which hyperconjugative interactions play a crucial role. In the case of borneol, the C–O bond of the alcohol and the hexasubstituted C–C bond of the bridge are antiperiplanar, thus maximizing hyperconjugative interactions between the electron-rich C–C σ

bond and the antibonding C–O σ^* bond, thereby lowering the bond energy of the C–O bond, as has also been shown experimentally.²⁶ In the case of isborneol, these bonds have a torsion angle of about 90°, which makes hyperconjugative interactions minimal. This electronic consideration, however, contradicts our experimental observations that isborneol reacts at 100 °C and borneol requires a higher temperature.

The other factor of influence is steric interactions. Steric interactions in borneol are smaller than in isborneol because of the configurational differences noted above. When assuming a Brønsted acidic E1 mechanism, protonation of the alcohol is not influenced in a significant manner by steric constraints because of the small size of a proton and also because elimination of water is not influenced significantly by sterics. This elimination can, however, release much steric strain in isborneol, thus making this a more favorable reaction compared with the same reaction in borneol. This consideration does agree with our experimental results. Depending on the exact mechanism, another factor based on steric interactions can also be of influence. An S_N2 -type reaction mechanism may be operative in this reaction. In this mechanism, a protonated alcohol group is substituted to a perchlorate ester. In this case, a backside attack on the α -carbon takes place, which is much more hindered in borneol compared with isborneol. This consideration would also explain the distinctly different reactivity of these two substrates.

Solid Acid Catalyst Activity. To benchmark the catalytic performance of Re_2O_7 against the performance of solid acids, the activity of a series of known solid acid catalysts was tested in the dehydration of α -terpineol. The low reactivity of the acidic sulfonated resins in this reaction is rather surprising, given the fact that *para*-toluenesulfonic acid, which can be considered the homogeneous analogue of these resins, was previously found to be active in the dehydration of benzylic alcohols.¹⁵ The amount of acidic sites present in these resins cannot explain their lack of activity either, since a total amount of 0.02 mmol of acid sites is present, on the basis of the dry weight exchange capacity of the resins, which is the same as the amount of rhenium atoms present in the rhenium-catalyzed reactions. A possible explanation could be found in the characteristics of the used acid resins. Since these are hydrophilic gel resins, they could collapse in hydrophobic solvents, such as toluene. This would render the acid sites unreachable and thus destroy the activity of the resins.

In the case of the tested zeolites, mass-transfer limitations seem to be of major importance under the mild conditions used for the dehydration reaction. ZSM-5 has the smallest pore size of the three tested zeolites and shows almost no activity. The low activity that is observed could be attributed to extra-framework acid sites. Zeolite Beta has much bigger pores and shows a much higher activity, while zeolite Y has the highest pore size and the highest activity of the three zeolites materials tested here. It is thus clear that activity is correlated with the pore size of the zeolite, indicating diffusion limitations of the substrate into the pores of the zeolites.

When considering the mesoporous material Al-MCM-41, the low activity cannot be attributed to its pore size, since it is an order of magnitude higher than that of the tested zeolites. The low activity could be attributed to its amorphous nature, which can cause a nonhomogeneous distribution of alumina in the framework and, consequently, a lower Brønsted acidity of the active sites.

The surprising inactivity of γ -alumina may be explained along a similar vein, in terms of insufficient Lewis acidity. Because the observed activity of the most active rhenium catalysts (Re_2O_7 , HReO_4 , $\text{ReIO}_2(\text{PPh}_3)_2$) could be attributed to their Lewis acidity (*vide supra*), the Lewis acidity of γ -alumina is likely of insufficient strength to catalyze the dehydration reaction under the given conditions.

Despite the fact that different solid acids with different structural factors and Si/Al ratios were tested, making direct comparison in terms of activity difficult, it is clear from these data that Re_2O_7 shows a higher activity on a weight-basis than any of the tested solid acids. From a selectivity viewpoint, the comparison is much more straightforward, showing the superior characteristics of Re_2O_7 in this reaction, yielding only limonene and terpinolene, whereas the solid acids yield a mixture of five products and a much lower total conversion and yield.

Recycling. During the seven recycling runs carried out for Re_2O_7 , a loss of activity in the dehydration reaction of α -terpineol was observed. This loss of activity upon recycling can be attributed to two factors: first of all, the method of recycling is prone to catalyst loss during decantation considering the small amounts of catalyst used in this reaction. The other factor is the (partial) solubility of Re_2O_7 in the reaction medium, either as dissolved Re_2O_7 or, because of reaction with water, as HReO_4 . The loss of activity after the first recycling is 31%, which is very comparable to the remaining activity of the filtrate after filtration in a separate experiment (27%), indicating that the partial solubility of Re_2O_7 is likely to be the major factor concerning the loss of activity during recycling.

CONCLUSIONS

We have reported on a series of rhenium-based catalyst systems that are able to dehydrate various alcohols to the corresponding olefins in a very efficient manner, with Re_2O_7 as the best performing catalyst. It was found that allylic, aliphatic, and homoallylic alcohols are readily dehydrated with Re_2O_7 under relatively mild conditions, using technical grade solvents and low reaction temperatures (100–150 °C). These conditions can also be applied to the dehydration of various terpene alcohols to yield the corresponding terpenes. As a proof of principle for its use in catalytic upgrading of essential oils, we have shown that this system is very effective in the upgrading of tea tree oil.

Comparison of Re_2O_7 with both sulfuric acid and several solid acids has shown that Re_2O_7 is the superior catalyst on the basis of both activity and selectivity. Furthermore, Re_2O_7 remains active in the dehydration of α -terpineol during seven runs of recycling. These combined results make Re_2O_7 a highly potent catalyst for the dehydration reaction and an interesting alternative for currently used acid catalysts. Ongoing experiments in our laboratory focus on the understanding of the mechanism of operation of Re_2O_7 and other rhenium-based catalysts in alcohol dehydration reactions and on further improving the activity and selectivity of these catalysts.

EXPERIMENTAL SECTION

General: All organic compounds were obtained from Sigma-Aldrich and used without further purification. $\text{ReIO}_2(\text{PPh}_3)_2$ and NBu_4ReO_4 were obtained from ABCR; Re metal, $\text{Re}(\text{CO})_5\text{Cl}$, $\text{ReOCl}_3(\text{PPh}_3)_2$, MTO, Re_2O_7 , KReO_4 , NH_4ReO_4 , Montmorillonite K10, Amberlite IR120 (hydrogen

form, 16 - 50 mesh), and Al-MCM-41 (mesostructured aluminosilicate) were obtained from Sigma-Aldrich; $\text{Re}_2(\text{CO})_{10}$, HReO_4 (76.5% solution in water), and Dowex 50WX8 (50–100 mesh) were obtained from Acros; and sulfuric acid (95–97%) was obtained from Merck, and all were used without further purification. γ -Alumina (250 m^2/g , 500 $\mu\text{m} < d < 850 \mu\text{m}$) was obtained from Engelhard. Zeolites H-Y (CBV 720) and H-Beta (CP811E-75) were obtained from Zeolyst. H-ZSM-5 was produced by calcination (500 °C for 3 h in air) of NH_4 -ZSM-5 (CBV 3024E), which was also obtained from Zeolyst. Technical toluene was obtained from Interchema and used without further purification. All reactions were performed in air.

GC analysis was performed on a Perkin-Elmer Autosystem XL gas chromatograph equipped with an Elite-17 column (30 m \times 0.32 mm \times 0.50 μm) and a flame ionization detector. Two temperature programs were used. For the nonbenzylic alcohol dehydration, the temperature was increased from 40 to 70 °C at 5 °C min^{-1} and subsequently to 250 °C at 30 °C min^{-1} , maintaining that temperature for 5 min. For the terpene alcohol dehydration, the temperature was increased from 100 to 250 °C at 10 °C min^{-1} . GC/MS analysis was performed on a Perkin-Elmer Autosystem XL with Turbomass Mass Spectrometry Upgrade and a J&W Scientific DB-17 column (30 m \times 0.32 mm \times 0.25 μm). Products were analyzed by comparison with genuine samples in GC and GC/MS. ^1H NMR spectra were recorded at 298 K on a Varian Oxford AS400 spectrometer at 400 MHz in toluene- d_8 .

Typical procedure for the dehydration of alcohols to olefins: To the catalyst was added a solution of substrate (2 mmol) and pentadecane as internal standard (250 μL , 192.3 mg) in toluene (10 mL). The reaction flask was sealed with a septum, placed in a preheated aluminum block heater at 100 °C, and magnetically stirred. Samples for GC analysis were taken by syringe, filtered over Florisil, and eluted with ethyl acetate. For the reactions analyzed by NMR, toluene- d_8 was used as the solvent, and the yield was determined against 1,3,5-trimethoxybenzene (0.67 mmol, 112.1 mg) as internal standard. When using a liquid catalyst, the same procedure was used, but the catalyst was added to the solution by Finnpiquette. For the reactions at 150 °C, the same procedure was used, but in an 18 mL Ace pressure tube (Sigma-Aldrich).

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Notes

The authors declare no competing financial interest.

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