



## Rhenium-catalyzed deoxygenation of epoxides without adding any reducing agent

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### ABSTRACT

This work reports a novel method for the deoxygenation of epoxides catalyzed by oxo-rhenium (V) and (VII) complexes without adding any reducing agent. This eco-friendly methodology was successfully applied to the deoxygenation of several epoxides with tolerance of different functional groups and high reusability of the catalysts  $\text{ReIO}_2(\text{PPh}_3)_2$  and  $\text{ReOCl}_3(\text{PPh}_3)_2$ .

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The deoxygenation of epoxides to alkenes is an important synthetic transformation in both organic synthesis and biological chemistry. The combination of epoxidation/deoxygenation would provide a useful protection/deprotection sequence for the multiple bond. However, the successful implementation of this strategy would largely depend on the effective deoxygenation of epoxides back to alkenes. Several methods have been developed to accomplish the deoxygenation of epoxides using several reagent systems such as  $\text{Cp}_2\text{TiCl}_2/\text{In}$ ,<sup>1</sup>  $\text{In}/\text{InCl}$ ,<sup>2</sup>  $\text{NbCl}_5/\text{Zn}$ ,<sup>3</sup>  $\text{ZrCl}_4/\text{NaI}$ ,<sup>4</sup>  $\text{CO}/\text{Au}$  nanoparticles,<sup>5,6</sup> alcohols/ $\text{Au}$ , or  $\text{Ag}$  nanoparticles.<sup>7</sup>

The high importance of the deoxygenation of epoxides justifies the search for novel, efficient, cheaper, chemoselective, and eco-friendly methodologies to carry out this reaction.

High-valent oxo-complexes, in particular, oxo-molybdenum<sup>8</sup> and oxo-rhenium<sup>9</sup> complexes are known for their abilities to catalyze oxygen transfer reactions. More recently, these oxo-complexes have also been successfully applied in the hydrosilylation of aldehydes and ketones,<sup>10,11</sup> in C–C,<sup>12</sup> C–S,<sup>12</sup> C–N,<sup>13</sup> and C–P<sup>14,15</sup> bond formation and also in several organic reactions such as the reduction of imines,<sup>16</sup> amides,<sup>17</sup> aromatic nitro compounds,<sup>18</sup> esters,<sup>19</sup> sulfoxides,<sup>20–25</sup> pyridine *N*-oxides,<sup>20</sup> and alkenes.<sup>26</sup>

The methods reported in the literature for deoxygenation of epoxides using oxo-rhenium complexes as catalysts involve the addition of an equivalent amount of phosphorous compounds,<sup>27–31</sup> dihydrogen ( $\text{H}_2$ , 80–300 psi) under high temperature (150 °C),<sup>32</sup> or sulfite<sup>33</sup> as the reductant.

In continuation of our studies on the use of high-valent oxo-complexes as excellent catalysts for organic reductions, in this work we report an easy and eco-friendly methodology for the deoxygenation of epoxides by oxo-rhenium (V) and (VII) complexes without adding any reducing agent or usual oxygen sink.

The deoxygenation of 4-chlorostyrene oxide was chosen as the model reaction for studying the influence of catalysts, and critical reaction parameters such as solvent and temperature (Tables 1 and 2).

In order to compare the catalytic activity of oxo-rhenium (V) and (VII) complexes, the deoxygenation of 4-chlorostyrene oxide was carried out in the presence of the catalysts  $\text{ReIO}_2(\text{PPh}_3)_2$ ,  $\text{ReOCl}_3(\text{PPh}_3)_2$ ,  $\text{ReOCl}_3(\text{dppm})$ ,  $\text{Re}_2\text{O}_7$ , and  $\text{CH}_3\text{ReO}_3$  (MTO) in refluxing toluene under air atmosphere (Table 1).

**Table 1**

Deoxygenation of 4-chlorostyrene oxide by oxo-rhenium (V) and (VII) complexes<sup>a</sup>

Entry	Catalyst	Catalyst (%)	Time	Yield <sup>b</sup> (%)
1	$\text{ReIO}_2(\text{PPh}_3)_2$	10	35 min	78
2	$\text{ReIO}_2(\text{PPh}_3)_2$	5	19 h	50
3	$\text{ReOCl}_3(\text{PPh}_3)_2$	10	30 min	67
4	$\text{Re}_2\text{O}_7$	10	30 min	62
5	$\text{ReOCl}_3(\text{dppm})$	10	1 h 30 min	59
6	MTO	10	24 h	49

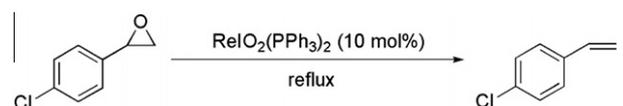
<sup>a</sup> All reactions were carried out with 1.0 mmol of epoxide.

<sup>b</sup> Isolated yield.

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**Table 2**  
Deoxygenation of 4-chlorostyrene oxide by  $\text{ReIO}_2(\text{PPh}_3)_2$  in different solvents<sup>a</sup>



Entry	Solvent	Temperature	Time	Yield (%)
1	Toluene	Reflux	35 min	78 <sup>b</sup>
2	Toluene	rt	24 h	12 <sup>c</sup>
3	THF	Reflux	2 h	76 <sup>c</sup>
4	$\text{CHCl}_3$	Reflux	24 h	56 <sup>c</sup>
5	Benzene	Reflux	7 h	35 <sup>c</sup>
6	$\text{CH}_2\text{Cl}_2$	Reflux	24 h	22 <sup>c</sup>
7	$\text{CH}_3\text{CN}$	Reflux	24 h	20 <sup>c</sup> (22) <sup>c,d</sup>

<sup>a</sup> All reactions were carried out with 0.5 mmol of epoxide.

<sup>b</sup> Isolated yield.

<sup>c</sup> Yields determined by  $^1\text{H}$  NMR using 4-(methylthio)benzaldehyde (0.5 mmol) as an internal standard.

<sup>d</sup> Yield of 4-chlorobenzaldehyde.

The best result was obtained using as the catalyst  $\text{ReIO}_2(\text{PPh}_3)_2$  (10 mol %), affording the 4-chlorostyrene in 78% yield after 35 min (Table 1, entry 1). Using only 5 mol % of this catalyst, the reaction required more time (19 h) and the alkene was obtained in moderate yield (Table 1, entry 2). The oxo-complexes  $\text{ReOCl}_3(\text{PPh}_3)_2$ ,  $\text{Re}_2\text{O}_7$ , and  $\text{ReOCl}_3(\text{dppm})$  also catalyzed the deoxygenation of 4-

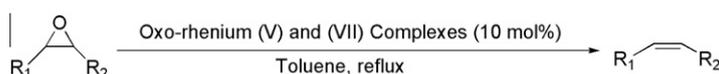
chlorostyrene oxide in moderate yields (Table 1, entries 3–5). Finally, the least reactive catalyst is MTO, producing the 4-chlorostyrene in only 49% yield after 24 h (Table 1, entry 6).

The influence of the solvent on the deoxygenation of epoxides was also explored (Table 2). Toluene was the best solvent at reflux temperature, affording the 4-chlorostyrene in 78% yield after only 35 min (Table 2, entry 1). At room temperature, the alkene was obtained in only 12% yield after 24 h (Table 2, entry 2). THF also gave good yield of 4-chlorostyrene, but the reaction required 2 h (Table 2, entry 3). In chloroform, benzene, and dichloromethane, the product was obtained in moderate to low yields (Table 2, entries 4–6). Finally, the deoxygenation of 4-chlorostyrene oxide in acetonitrile gave a mixture of 4-chlorostyrene (20%) and 4-chlorobenzaldehyde (22%) (Table 2, entry 7).

To evaluate the general applicability of this novel methodology, the deoxygenation of several epoxides using 10 mol % of  $\text{ReIO}_2(\text{PPh}_3)_2$ ,  $\text{ReOCl}_3(\text{PPh}_3)_2$ , and  $\text{Re}_2\text{O}_7$  in refluxing toluene was explored (Table 3).<sup>34</sup> Generally, moderate to good yields of alkenes were obtained. Both terminal and internal epoxides were deoxygenated by this novel method.

We observed that the deoxygenation of the *cis*-stilbene oxide produced only *cis*-stilbene and the *trans*-stilbene oxide afforded only the *trans*-stilbene (Table 3, entries 10–13). However, the deoxygenation of the commercial mixture of *cis* and *trans* ethyl 3-phenyl-2-oxiranecarboxylate, only gave the isomer ethyl (2*E*)-3-phenyl-2-propenoate (Table 3, entries 4–6).

**Table 3**  
Deoxygenation of epoxides by oxo-rhenium (V) and (VII) complexes<sup>a</sup>



Entry	Substrate	Product	Catalyst	Time	Yield <sup>b</sup>
1			$\text{ReIO}_2(\text{PPh}_3)_2$	35 min	78
2			$\text{ReOCl}_3(\text{PPh}_3)_2$	30 min	67
3			$\text{Re}_2\text{O}_7$	30 min	62
4			$\text{ReIO}_2(\text{PPh}_3)_2$	2 h 15 min	73
5			$\text{ReOCl}_3(\text{PPh}_3)_2$	1 h	79
6			$\text{Re}_2\text{O}_7$	3 h	64
7			$\text{ReIO}_2(\text{PPh}_3)_2$	35 min	70
8			$\text{ReOCl}_3(\text{PPh}_3)_2$	35 min	65
9			$\text{Re}_2\text{O}_7$	2 h	45
10			$\text{ReIO}_2(\text{PPh}_3)_2$	15 min	68
11			$\text{ReOCl}_3(\text{PPh}_3)_2$	40 min	54
12			$\text{ReIO}_2(\text{PPh}_3)_2$	25 min	63
13			$\text{ReOCl}_3(\text{PPh}_3)_2$	20 min	57
14			$\text{ReIO}_2(\text{PPh}_3)_2$	30 min	67
15			$\text{ReOCl}_3(\text{PPh}_3)_2$	1 h	48
16			$\text{ReIO}_2(\text{PPh}_3)_2$	35 min	58 <sup>c</sup>
17			$\text{ReOCl}_3(\text{PPh}_3)_2$	1 h 30 min	40 <sup>c</sup>
18			$\text{ReIO}_2(\text{PPh}_3)_2$	24 h	51 <sup>c</sup>
19			$\text{ReOCl}_3(\text{PPh}_3)_2$	24 h	30 <sup>c</sup>

<sup>a</sup> All reactions were carried out with 1.0 mmol of epoxide and 10.0 mol % of catalyst.

<sup>b</sup> Isolated yield.

<sup>c</sup> Yields determined by  $^1\text{H}$  NMR using 4-(methylthio)benzaldehyde (1.0 mmol) as an internal standard.

A variety of functional groups such as –Cl, –Br, –F, –NO<sub>2</sub>, and ester remained unaffected during deoxygenation of the corresponding epoxides (Table 3, entries 1–9, 14, 15, 18, and 19). The high chemoselectivity of this methodology is also demonstrated in the deoxygenation of 4-chlorostyrene oxide performed in the presence of other functional compounds such as benzophenone, *N*-(4-formylphenyl)acetamide, dibenzyl sulfoxide, bis-(4-chlorophenyl)sulfone, 4-(trifluoromethyl)benzotrile, without affecting the functional groups ketone, aldehyde, amide, sulfoxide, sulfone, or cyano. However, these reductions required more time (1.5–2 h).

The deoxygenation of the substrates 4-chlorostyrene oxide, ethyl 3-phenyl-2-oxiranecarboxylate, and 4-nitrostyrene oxide catalyzed by Re<sub>2</sub>O<sub>7</sub> (10 mol %) afforded the corresponding alkenes in 45–72% yield (Table 3, entries 3, 6, and 9). Nevertheless, some exceptions were observed in the deoxygenation of styrene oxide, and *cis*- or *trans*-stilbene oxides with this catalyst, producing a mixture of the alkene and benzaldehyde in low yields.

The reusability of oxo-rhenium complexes ReO<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (10 mol %) and ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> (10 mol %) was evaluated using 4-chlorostyrene oxide as the test substrate, by the sequential addition of fresh substrate to the reaction mixture. The reactions were followed by <sup>1</sup>H NMR, and the results obtained demonstrate that the complex ReO<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> can be reused in 15 cycles and the catalyst ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> in 5 cycles with the same catalytic activity.

In contrast to the simplicity of this novel methodology, the mechanism of the reaction is still unknown. However, when the catalytic deoxygenation of styrene oxide was monitored by <sup>1</sup>H NMR, we observed the formation of 1-phenyl-1,2-ethanediol, which disappears at the end of the reaction. The formation of the diol should result from the hydrolytic ring opening promoted by the Lewis acidic character of oxo-rhenium complexes. Then, we investigated the deoxygenation of 1-phenyl-1,2-ethanediol with ReO<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>, and Re<sub>2</sub>O<sub>7</sub> under the same catalytic conditions and we observed the deoxygenation of the diol with the formation of styrene, in moderate yields. This result also suggests that this method can be explored for the deoxygenation of diols to the corresponding alkenes.

In comparison to the other procedures catalyzed by oxo-rhenium complexes reported in the literature,<sup>27–33</sup> this new method has fast reaction times; is also more economic, easy, and eco-friendly, minimizing the use and generation of hazardous substances. Furthermore, the reactions can be carried out under air atmosphere with readily available laboratory equipment, in contrast to catalytic hydrogenation,<sup>32</sup> which demands handling of hydrogen gas and high-pressure equipment.

In conclusion, we have developed a novel, practical, and eco-friendly method for the deoxygenation of epoxides to the corresponding alkenes catalyzed by oxo-rhenium (V) and (VII) complexes with the following advantages: (1) moderate to good catalytic activity; (2) absence of a reducing agent; (3) high chemoselectivity; (4) use of commercial and easy-to-handle catalysts; (5) applicability to a variety of epoxides; (6) high reusable capacity. To the best of our knowledge, this is the first example of the deoxygenation of epoxides catalyzed by oxo-rhenium complexes without adding a reducing agent. All these features make this procedure one of the easiest, practical and eco-friendly procedure for the deoxygenation of epoxides reported in the literature.

Further studies to improve the yields of the deoxygenation through catalyst modifications and mechanistic studies are now in progress in our group.

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- In a typical experiment, to a solution of oxo-rhenium complex (10.0 mol %) in toluene (3 mL) was added the epoxide (1.0 mmol). The reaction mixture was heated at reflux temperature under air atmosphere (the reaction times are indicated in the Tables 1–3) and the progress of the reaction was monitored by TLC or <sup>1</sup>H NMR. Upon completion, the reaction mixture was evaporated and purified by silica gel column chromatography with *n*-hexane to afford the alkenes.