

Short Communication

Efficient and selective oxidation of alcohols catalyzed by oxo-rhenium complexes



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ABSTRACT

This work reports the catalytic activity of several oxo-rhenium complexes in the oxidation of alcohols, using a sulfoxide as oxidant agent. The catalytic system bis(4-chlorophenyl) sulfoxide/ $\text{ReOCl}_3(\text{PPh}_3)_2$ (10 mol%) proved to be efficient for the oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones. The primary alcohols are selectively oxidized to the corresponding aldehydes with no further oxidation to acids. The bis(4-chlorophenyl) sulfide, isolated as by-product in high yields, can be used as a substrate in other reactions or can be oxidized and reused in this procedure.

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1. Introduction

The oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones is a fundamental process in organic chemistry. In particular, the oxidation of primary alcohols to aldehydes is very important since they find wide applications as intermediates in chemical and pharmaceutical industries. Traditionally, the oxidation of alcohols is carried out using stoichiometric inorganic oxidants such as Cr(VI) based reagents, which generates large amount of heavy metal waste [1].

The Swern oxidation (using DMSO coupled with the electrophile oxalyl chloride) is also an efficient and widely used method for the oxidation of primary and secondary alcohols [2,3]. However, these reagents bring some disadvantages: the by-product dimethyl sulfide is volatile (bp 37 °C) and has an unpleasant smell; the electrophile oxalyl chloride is moisture sensitive, toxic and its vapors are powerful irritants, particularly to the respiratory system; the activation of DMSO can be violent and exothermic, and it must occur at low temperatures (−60 °C). Several modifications on the Swern methodology have been accomplished in order to overcome some of these disadvantages [4–8].

Among several metal transition complexes that have been used for the oxidation of alcohols, oxo-vanadium [9,10], oxo-molybdenum [11–13] and oxo-rhenium [14] complexes proved to be efficient catalysts in the presence of molecular oxygen or using a hydroperoxide compound as oxidant agent. Only few studies have also been reported for the oxidation of alcohols with DMSO catalyzed by oxo-molybdenum or -rhenium complexes [15–18].

Recently, we reported a novel method for the oxidation of benzyl alcohol to the corresponding aldehydes catalyzed by the oxo-complexes MoO_2Cl_2 , $\text{MoO}_2(\text{acac})_2$, $\text{VO}(\text{acac})_2$, WO_2Cl_2 and HReO_4 via oxygen transfer from sulfoxide [19]. The results obtained demonstrate that HReO_4 is a very efficient catalyst for the selective oxidation of benzyl alcohols to the corresponding aldehydes, with no further oxidation to acids. However, this catalyst is not very effective for the oxidation of secondary alcohols.

In this work we decide to explore the catalytic activity of other oxo-rhenium complexes in the oxidation of primary and secondary alcohols, using a sulfoxide as oxidant agent.

2. Experimental

2.1. General

All of the reactions were carried out in air and without any dry solvents. Alcohols, sulfoxides and catalysts were obtained from commercial suppliers and were used without further purification. $\text{ReO}_2(\text{PPh}_3)_2$ [20] and $\text{ReOBr}_3(\text{PPh}_3)_2$ [21] were prepared using the method reported in the literature. Flash chromatography was performed on MN Kieselgel 60 M of 230–400 mesh. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker Avance II 400 MHz and 300 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) downfield from an internal standard.

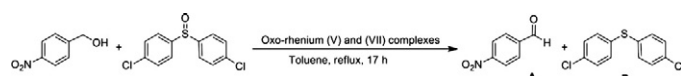
2.2. General procedure for the oxidation of alcohols catalyzed by $\text{ReOCl}_3(\text{PPh}_3)_2$ using bis(4-chlorophenyl) sulfoxide as oxidant agent

To a solution of $\text{ReOCl}_3(\text{PPh}_3)_2$ (0.083 g, 0.1 mmol) in toluene (3 mL) was added the bis(4-chlorophenyl) sulfoxide (0.271 g, 1 mmol) and the

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Table 1

Oxidation of alcohols catalyzed by oxo-rhenium (V) and (VII) complexes using bis(4-chlorophenyl) sulfoxide as oxidant agent^a.



Entry	Catalyst	Catalyst (mol%)	Yield A/B (%) ^b
1	ReOCl ₃ (PPh ₃) ₂	10	93/94
2	ReOCl ₃ (PPh ₃) ₂	5	55/63
3	ReOCl ₃ (PPh ₃) ₂	2	41/62
4	Re ₂ O ₇	10	88/80 (10) ^c
5	ReOBr ₃ (PPh ₃) ₂	10	82/90
6	ReIO ₂ (PPh ₃) ₂	10	70/85 (25) ^d
7	ReOCl ₃ (dppm)	10	55/69 (45) ^d
8	MTO	10	No reaction
9	–	–	No reaction

^a All reactions were carried out with 1.0 mmol of sulfoxide and 1.0 mmol of alcohol.

^b Isolated yield.

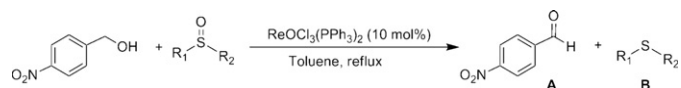
^c Sulfoxide recovered.

^d Alcohol recovered.

alcohol (1.0 mmol). The reaction mixture was heated at reflux temperature in air (the reaction times are indicated in Tables 1–4) and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was evaporated and purified by silica gel column chromatography with *n*-hexane to afford carbonyl compounds and bis(4-chlorophenyl) sulfide, which are all known compounds and their ¹H NMR and ¹³C NMR data are consistent with those of the commercial products.

Table 2

Oxidation of 4-nitrobenzyl alcohol catalyzed by ReOCl₃(PPh₃)₂ using different sulfoxides as oxidant agents^a.



Entry	Sulfoxide	Time (h)	Yield (%) ^b (A/B)
1		17	93/94
2		17	91/94
3		17	85/87
4		17	81/91 (8) ^c
5		24	70/– (26) ^c
6		17	No oxidation
7	–	24	No oxidation

^a All reactions were carried out with 1.0 mmol of sulfoxide and 1.0 mmol of alcohol.

^b Isolated yield.

^c Alcohol recovered.

3. Results and discussion

In order to find the best catalytic conditions for the oxidation of alcohols, initially we carried out several preliminary studies using different oxo-rhenium complexes, sulfoxides, solvents and temperatures (Tables 1–3).

3.1. Effect of the catalyst

The oxidation of alcohols was explored with the test substrate 4-nitrobenzyl alcohol in the presence of the oxo-rhenium complexes ReOCl₃(PPh₃)₂, ReOBr₃(PPh₃)₂, ReIO₂(PPh₃)₂, ReOCl₃(dppm), Re₂O₇, and CH₃ReO₃ (MTO) using bis(4-chlorophenyl) sulfoxide as an oxidant agent. The reactions were carried out in refluxing toluene (Table 1), and the progress of the oxidations was monitored by thin layer chromatography. The best results were obtained with ReOCl₃(PPh₃)₂ (10 mol%), affording 4-nitrobenzaldehyde in 93% yield after 17 h (Table 1, entry 1). Using only 5 mol% or 2 mol% of ReOCl₃(PPh₃)₂ the reactions gave moderate yields of aldehyde (Table 1, entries 2 and 3). The oxo-rhenium complexes Re₂O₇, ReOBr₃(PPh₃)₂, and ReIO₂(PPh₃)₂ produced good yields of the aldehyde (88–70%) (Table 1, entries 4–6) and ReOCl₃(dppm) only afforded moderate yield of the product (55%) (Table 1, entry 7). Finally, no oxidation was observed with MTO (Table 1, entry 8) and in the absence of catalyst (Table 1, entry 9).

3.2. Effect of the oxidant agent

Several sulfoxides were also tested as oxidant agents in the reaction of 4-nitrobenzyl alcohol catalyzed by 10 mol% of ReOCl₃(PPh₃)₂ in reflux of toluene. Among all of the sulfoxides, the reaction with bis(4-chlorophenyl) sulfoxide produced the best yield (93%) of 4-nitrobenzaldehyde (Table 2, entry 1). Using the sulfoxides di-*p*-tolyl sulfoxide, diphenyl sulfoxide and 4-nitrophenyl phenyl sulfoxide as oxidant agents, good yields of 4-nitrobenzaldehyde were also obtained (91–81%) (Table 2, entries 2–4). In the presence of DMSO, 4-nitrobenzyl alcohol was oxidized in 70% yield (Table 2, entry 5), and using dibenzyl sulfoxide or in absence of sulfoxide, no oxidation of the alcohol was observed (Table 2, entries 6 and 7). Good yields of the sulfides were also isolated (Table 2, entries 1–4).

3.3. Effect of solvent and temperature

The reaction between the test substrate 4-nitrobenzyl alcohol and the oxidant agent bis(4-chlorophenyl) sulfoxide catalyzed by ReOCl₃(PPh₃)₂ (10 mol%) was studied in different solvents. Toluene proved to be the best solvent at reflux temperature, affording 4-nitrobenzaldehyde in 93% yield and 94% of sulfide (Table 3, entry 1). At room temperature, this oxidation only gave moderate yield of the aldehyde (Table 3, entry 2). In benzene, dichloromethane and chloroform the aldehyde was obtained in 56–79% yields and the sulfide was obtained in 77–82% yields (Table 3, entries 3–5). In contrast, low yields of aldehydes (5–27%) were obtained in acetonitrile and THF (Table 3, entries 6 and 7). However, the sulfide was obtained in good yields from these solvents (75–94%).

3.4. Scope and limitations

In order to assess the scope and limitations of this methodology, we decided to study the oxidation of several primary and secondary alcohols using bis(4-chlorophenyl) sulfoxide as oxidant agent catalyzed by 10 mol% of ReOCl₃(PPh₃)₂ in reflux of toluene (Table 4).

The oxidation of primary alcohols gave selectively the corresponding aldehydes in good to excellent yields with no further oxidation to acids. 4-Nitrobenzaldehyde, methyl 4-formylbenzoate, 4-fluorobenzaldehyde, 4-iodobenzaldehyde, 4-bromobenzaldehyde,

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