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ARTICLE

Deoxygenation of Carbonyl Compounds using an Alcohol as Efficient Reducing Agent Catalyzed by Oxo-rhenium Complexes

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This work describes the first methodology for the deoxygenation of carbonyl compounds using an alcohol as green solvent/reducing agent catalyzed by oxo-rhenium complexes. The system 3-pentanol/ReOCl₃(SMe₂)(OPPh₃) was successfully employed in the deoxygenation of several aryl ketones to the corresponding alkenes and also in the deoxygenation of aryl aldehydes to alkanes with moderate to excellent yields. The catalyst ReOCl₃(SMe₂)(OPPh₃) can also be used in several catalytic cycles with good activity.

Introduction

During the last few years, many efforts were carried out to discover and to develop new green chemical processes for the deoxygenation of organic compounds. In particular, the reductive deoxygenation of carbonyl compounds to the corresponding alkanes or alkenes has attracted considerable attention given its many applications in fine-chemical synthesis and pharmaceutical industry.¹ The deoxygenation of carbonyl compounds from biomass resources is also an important process and has been a key target in chemical engineering and biofuel production, due to the concerns about diminishing fossil fuel sources, increasing fuel prices, global warming, and environmental pollution.^{2,3}

Generally, the reduction of carbonyl group to the corresponding methylene derivative can be carried out by chemical methods such as Clemmensen reduction,⁴ Wolff-Kishner reduction,⁵ NaBH₄-CF₃CO₂H,⁶ HI-Phosphorus,⁷ TMSCl-Zn,⁸ GaCl₃-Me₂SiClH,⁹ InCl₃-TMSCl,¹⁰ PMHS-Pd/C,¹¹ PMHS-Pd(OAc)₂,¹² PMHS-B(C₆F₅)₃,¹³ InBr₃-Et₃SiH,¹⁴ Raney nickel-2-propanol.¹⁵ However, due to the harsh conditions of some of these methodologies, they are restricted for the deoxygenation of compounds containing other functional groups. There are also number of catalytic protocols for the deoxygenation of carbonyls employing molecular hydrogen (H₂) using the catalysts Pd-Choline-based ionic liquids,¹⁶ Cu/SiO₂,¹⁷ or Cu₃₀Cr₁₀/γ-Al₂O₃.¹⁸ Although, H₂ constitutes the most atom-efficient and green reducing agent, its use is generally associated with high pressure, special equipment and safety precautions to minimize the explosion risk.

In contrast to the several methods reported in the literature for the deoxygenation of carbonyl compounds to

alkanes, there are very few methodologies for the selective direct deoxygenation of ketones to alkenes. One example consist in the method reported by Carney which is a modification of the Clemmensen reduction using amalgamated zinc and formic acid in reflux of ethanol.¹⁹ The Shapiro reaction also provides a convenient method to convert ketones into a plethora of olefinic substances in high yields, by reaction of ketones with (phenylsulfonyl)hydrazine, forming the corresponding hydrazones, which react with a strong base, such as *n*-butyllithium, producing the olefins.²⁰ The deoxygenation of tetralones and indanones to the corresponding alkenes can also be afforded using an alcohol and acid catalysis.²¹

Oxo-rhenium complexes have been applied in the deoxygenation of many organic compounds²² such as sulfoxides,²³ epoxides,²⁴ aromatic nitro compounds,²⁵ *N*-oxides²⁶ and alcohols.^{24d,24e,27} Very recently, we developed the first methodology for the direct reductive deoxygenation aryl ketones to the corresponding alkanes or to a mixture of alkane and alkene using the systems PhSiH₃/ReOCl₃(SMe₂)(OPPh₃) and PhSiH₃/ReOCl₃(PPh₃)₂.²⁸ After, our group developed another very efficient method for the selectively deoxygenation of aryl ketone to alkenes using MoO₂Cl₂(H₂O)₂ as catalyst and PhSiH₃ as reducing agent.²⁹

In the last years the use of alcohols as green reducing agents has attracted considerable attention. They proved to be effective reducing agents for the deoxydehydrogenation of glycols,^{27b,30} deoxygenation of sulfoxides³¹ and nitro compounds^{31a} in the presence of oxo-rhenium and oxo-molybdenum complexes. To best of our knowledge, there are no reports of the use of alcohols as reducing agents for the direct deoxygenation of carbonyl compounds catalyzed by oxo-complexes.

In order to develop new catalyst/reductant systems with optimum efficiency, selectivity, economy, and ecofriendly we decided to investigate the deoxygenation of ketones and aldehydes using an alcohol as green solvent/reducing agent and an oxo-rhenium complex as catalyst.

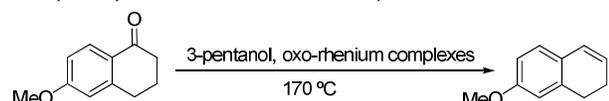
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Results

The catalytic activity of several oxo-rhenium complexes was compared in the deoxygenation of the test substrate 6-methoxytetralone using 3-pentanol as reducing agent (Table 1). The oxo-rhenium complex $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ proved to be the more efficient catalyst at 170 °C under air atmosphere. The best result was obtained using 10 mol% of $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$, affording the alkene in 98% yield after 6 h (Table 1, entry 1). In the presence of 5 mol% of this catalyst, the alkene was also formed in good yield, but the reaction required 17 h (Table 1, entry 2). Low yield of alkene was obtained using 2 mol% of $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ (Table 1, entry 3). The reaction catalyzed by the oxo-complex $\text{ReOCl}_3(\text{PPh}_3)_2$ (5 mol%) gave the alkene in 67% yield (Table 1, entry 4). Moderate to low yields of alkene were observed in the deoxygenation catalyzed by complexes $\text{ReOBr}_3(\text{PPh}_3)_2$, $\text{ReO}_2(\text{PPh}_3)_2$, $\text{ReOCl}_3(\text{dppm})$ and MTO (Table 1, entries 5-8). No reaction was observed in the presence of NaReO_4 and in the absence of catalyst (Table 1, entry 9 and 10).

The deoxygenation of 6-methoxytetralone catalyzed by $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ (5 mol%) was also investigated using different secondary and primary alcohols as reducing agents (Table 2). 3-Pentanol was the best reducing agent for this reaction, affording the alkene with 84% yield at 170 °C under air atmosphere (Table 2, entry 1). At reflux temperature of 3-pentanol (120 °C) the reaction did not occur (Table 2, entry

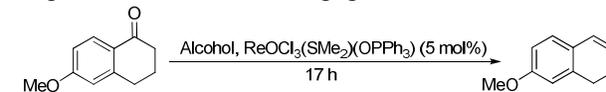
Table 1 Direct reductive deoxygenation of 6-methoxytetralone catalyzed by different oxo-rhenium complexes^a



| Entry | Catalyst | Catalyst (mol%) | Time | Yield (%) ^b |
|-------|---|-----------------|------|------------------------|
| 1 | $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ | 10 | 6 | 98 |
| 2 | $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ | 5 | 17 | 84 (5) ^c |
| 3 | $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ | 2 | 17 | 37 (42) ^c |
| 4 | $\text{ReOCl}_3(\text{PPh}_3)_2$ | 5 | 17 | 67 |
| 5 | $\text{ReOBr}_3(\text{PPh}_3)_2$ | 5 | 17 | 39 (54) ^c |
| 6 | $\text{ReO}_2(\text{PPh}_3)_2$ | 5 | 17 | 33 (57) ^c |
| 7 | $\text{ReOCl}_3(\text{dppm})$ | 5 | 17 | 30 (70) ^c |
| 8 | MTO | 5 | 17 | 13 (86) ^c |
| 9 | NaReO_4 | 5 | 17 | No reaction |
| 10 | Without catalyst | – | 17 | No reaction |

^aThe reactions were carried out with 0.5 mmol of 6-methoxytetralone and 2 mL of 3-pentanol. ^bYield determined by ¹H NMR spectroscopy using 1,2-dimethoxyethane as internal standard. ^cSubstrate

Table 2 Direct reductive deoxygenation of 6-methoxytetralone using different alcohols as reducing agents^a

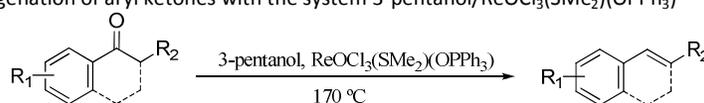


| Entry | Alcohol | Temp. (°C) | Yield (%) ^b |
|-------|-----------------|------------|--|
| 1 | 3-pentanol | 170 | 84 (5) ^c |
| 2 | 3-pentanol | 120 | No reaction |
| 3 | 2-pentanol | 170 | 75 |
| 4 | 1-butanol | 170 | 47 (53) ^c |
| 5 | 3-hexanol | 170 | 39 (35) ^d (18) ^e |
| 6 | 2-butanol | 170 | No reaction |
| 7 | glycerol | 200 | No reaction |
| 8 | Ethylene glycol | 170 | No reaction |
| 9 | 2-octanol | 170 | No reaction |
| 10 | 2-propanol | 170 | No reaction |
| 11 | Ethanol | 170 | No reaction |
| 12 | Methanol | 170 | No reaction |

^aThe reactions were carried out with 0.5 mmol of 6-methoxytetralone and 2 mL of alcohol. ^bYields determined by ¹H NMR spectroscopy using 1,2-dimethoxyethane as internal standard. ^cSubstrate. ^dYield of Alkane. ^eYield of Alcohol

2). Good yield of alkene (75%) was also observed in the deoxygenation of 6-methoxytetralone with 2-pentanol (Table 2, entry 3). The reaction using 1-butanol as reducing agent only led to moderate yield of alkene (Table 2, entry 4). An interesting result was observed in the deoxygenation of 6-methoxytetralone with 3-hexanol that produced the alkene in 39% yield, along with 35% yield of the alkane and 18% yield of alcohol (Table 2, entry 5). Finally, the reductions performed with glycerol, ethylene glycol, 2-butanol and 2-octanol and with small alcohols such as 2-propanol, ethanol and methanol did not occur (Table 2, entries 6-12). As reported previously by Toste,^{30a} the reactivity of the different alcohols was dependent on both size and structure of the alcohol. In general secondary alcohols gave higher yields than primary alcohols owing to decreased by-product formation. The reactivity increased as the carbon chain length of alcohol increased, presumably because the strong coordination of multiple alcohol molecules to the rhenium center was prevented.

In order to explore the scope and the limitations of this novel method, we investigated the deoxygenation of several ketones and aldehydes with the system 3-pentanol/ $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ at 170 °C under air atmosphere in a closed Schlenk equipped with a J-Young tap, without using any special pressure-controlling equipment (Tables 3 and 4). The progress of the reactions was monitored by thin layer chromatography and by ¹H NMR spectroscopy. The best yield of alkene (96%) was obtained in the deoxygenation of 5-methoxytetralone in the presence of 10

Table 3 Direct reductive deoxygenation of aryl ketones with the system 3-pentanol/ReOCl₃(SMe₂)(OPPh₃)^a

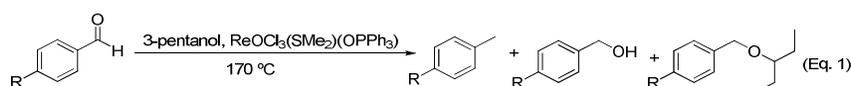
| Entry | Ketone | Product | Catalyst (mol%) | Time (h) | Yield (%) |
|-------|--------|---------|-----------------|----------|------------------------|
| 1 | | | 10 | 6 | 96 ^c |
| 2 | | | 5 | 17 | 90 ^c |
| 3 | | | 10 | 6 | 87 ^c |
| 4 | | | 5 | 17 | 82 (5) ^{d,c} |
| 5 | | | 10 | 17 | 88 ^c |
| 6 | | | 5 | 17 | 44 (62) ^{d,b} |
| 7 | | | 10 | 17 | 88 (10) ^{d,b} |
| 8 | | | 10 | 40 | 36 (64) ^{e,b} |
| 9 | | | 10 | 48 | 55 (45) ^{d,b} |
| 10 | | | 10 | 17 | 65 ^b |
| 11 | | | 10 | 40 | 78 (20) ^{d,c} |
| 12 | | | 10 | 40 | 50 (40) ^{d,c} |
| 13 | | | 10 | 40 | 50 (25) ^{f,c} |
| 14 | | | 10 | 40 | 65 (35) ^{d,c} |

^aThe reactions were carried out with 0.5 mmol of ketone and 2 mL of 3-pentanol. ^bYields determined by ¹H NMR spectroscopy using 1,2-dimethoxyethane as the internal standard. ^cIsolated yield. ^dSubstrate. ^eYield of alcohol. ^fYield of ether.

mol% of $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ after 6 h (Table 3, entry 1). Using only 5 mol% of this catalyst, the alkene was afforded in 90% yield after 17 h (Table 3, entry 2). Both reactions of 6-methoxytetralone with 10 mol% or with 5 mol% of $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ produced good yields of alkene, but the deoxygenation with 10 mol% of catalyst was much faster (6 h) (Table 3, entries 3 and 4). In contrast, the reduction of the 7-methoxytetralone required 10 mol% of $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ to give 88% yield of alkene (Table 3, entry 5). The alkene was also obtained in good yield (88%) in the reaction of α -tetralone with 10 mol% of $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ (Table 1, entry 7). Interestingly, the deoxygenation of the β -tetralone also produced the alkene in 36% yield, along with 64% yield of the alcohol (Table 3, entry 8).

In the reaction of 4-methyltetralone was obtained the alkene in 55% yield after 48 h using 10 mol% of $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ (Table 3, entry 9).

The deoxygenation of chromanone was also investigated and gave the alkene in 65% yield (Table 3, entry 10). The ketones deoxyanisoin and deoxybenzoin were also deoxygenated, affording the corresponding alkenes in 78% and 50% yield,



respectively (Table 3, entries 11 and 12). Curiously, the reaction of 4'-chloro-2-phenylacetophenone, under the same reaction conditions, produced the alkane in 50% yield, along with 25% yield of the ether, resulting of the reaction with 3-pentanol (Table 3, entry 13). Finally, the system 3-pentanol/ $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ was also applicable to the deoxygenation of isobutyrophenone, giving the alkene (65% yield) (Table 3, entry 14).

The efficiency of the system 3-pentanol/ $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ was also tested in the deoxygenation of several aryl aldehydes (Table 4). In these reactions were obtained the corresponding alkenes, and in certain cases, it was observed the formation of the primary alcohol and the ethers (Eq. 1).

The best result was obtained in the reaction of 2,4-dichlorobenzaldehyde producing 2,4-dichlorotoluene in 91% yield (Table 4, entry 1). The reduction of

Table 4 Direct reductive deoxygenation of aldehydes with the system 3-pentanol/ $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)^a$

| Entry | Aldehyde | Product | Time (h) | Yield (%) |
|-------|----------|---------|----------|-------------------------------------|
| 1 | | | 17 | 91 ^c |
| 2 | | | 17 | 75 (19) ^{d,c} |
| 3 | | | 17 | 66 ^c |
| 4 | | | 40 | 50 (40) ^{d,b} |
| 5 | | | 17 | 40 (50) ^{e,b} |
| 6 | | | 17 | 79 ^c (10) ^{f,b} |
| 7 | | | 17 | 79 (16) ^{f,c} |

^aThe reactions were carried out with 0.5 mmol of aldehyde and 2 mL of alcohol. ^bYields determined by ¹H NMR spectroscopy using 1,2-dimethoxyethane as the internal standard. ^cIsolated yields. ^dYield of ether. ^eYield of alcohol. ^fYield of alkane.

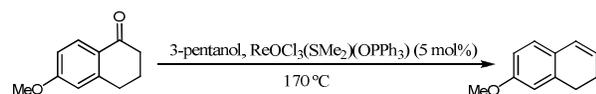
4-bromobenzaldehyde with this system gave 4-bromotoluene in 75% yield and 19% yield of ether (Table 3, entry 2). The deoxygenation of 4-chlorobenzaldehyde afforded 4-chlorotoluene as the major product (66% yield), along with the residual amounts of 4-chlorobenzyl alcohol and ether (Table 3, entry 3). Similarly, from 4-fluorobenzaldehyde was obtained 4-fluorotoluene in 50% yield and the ether in 40% yield (Table 4, entry 4). In contrast, the reaction of methyl 4-formylbenzoate produced as the major product the alcohol methyl 4-(hydroxymethyl)benzoate in 50% yield and the deoxygenated product methyl 4-methylbenzoate in 40% yield (Table 4, entry 5). Finally, from the reactions of the 4-(methylthio)benzaldehyde and 4-methylbenzaldehyde, containing electron-donating groups, were obtained the corresponding ethers with excellent yields and the alkanes in low yields (Table 4, entries 6 and 7). The results obtained demonstrate that the aldehydes with electron-withdrawing groups led to best yields of alkanes.

In order to study the possible use of the complex $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ as catalyst in several cycles, we carried out successive reactions by sequential addition of fresh substrate 6-methoxytetralone to the reaction mixture, using 3-pentanol as reducing agent. The reactions were monitored by ^1H NMR spectroscopy and the results obtained showed that $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ can be used in the first two catalytic cycles with excellent yields and in 3th cycle with good yield (Table 5).

The catalytic activity of the oxo-complex $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ was also studied by ^1H NMR spectroscopy, in several cycles in the deoxygenation of 2,4-dichlorobenzaldehyde by successive additions of fresh substrate to the reaction mixture, showing that this catalyst can be used in at least 8 cycles with excellent to good yields (Table 6).

The formation of the alcohol in some reductions suggests that it could be an intermediate in the deoxygenation of the carbonyl compound. This result indicates that the deoxygenation of the carbonyl compounds should proceed in two steps, where the carbonyl compound is first reduced to the alcohol, followed by deoxygenation to the alkene or the

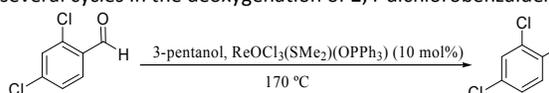
Table 5 Use of the complex $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ as catalyst in several cycles in the deoxygenation of 6-methoxytetralone^a



| Catalytic cycle | Time (h) | Yield (%) ^b |
|-----------------|----------|------------------------|
| 1 | 17 | 84 |
| 2 | 24 | 81 |
| 3 | 24 | 70 |

^aThe reactions were carried out by successive additions of 0.5 mmol of 6-methoxytetralone to the reaction mixture in 3 mL of 3-pentanol. ^bYields determined by ^1H NMR spectroscopy using 1,2-dimethoxyethane as the internal standard.

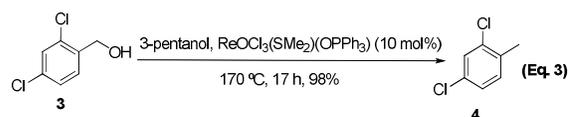
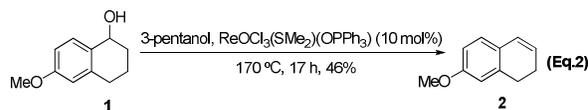
Table 6 Use of the complex $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ as catalyst in several cycles in the deoxygenation of 2,4-dichlorobenzaldehyde^a



| Catalytic cycle | Time (h) | Yield (%) ^b |
|-----------------|----------|------------------------|
| 1 | 17 | 91 |
| 2 | 24 | 91 |
| 3 | 24 | 90 |
| 4 | 24 | 82 |
| 5 | 24 | 89 |
| 6 | 24 | 88 |
| 7 | 24 | 85 |
| 8 | 24 | 71 |

^aThe reactions were carried out by successive additions of 0.5 mmol of 2,4-dichlorobenzaldehyde to reaction mixture in 3 mL of 3-pentanol. ^bYields determined by ^1H NMR spectroscopy using 1,2-dimethoxyethane as the internal standard.

alkane. To examine this hypothesis we decide to carry out the deoxygenation of alcohols **1** and **3** with the system 3-pentanol/ $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ (10 mol%), obtaining the corresponding alkene and alkane in 46% and 98% yields, respectively (Eqs 2 and 3).



The temporal progression of the deoxygenation of 2,4-dichlorobenzaldehyde with the system

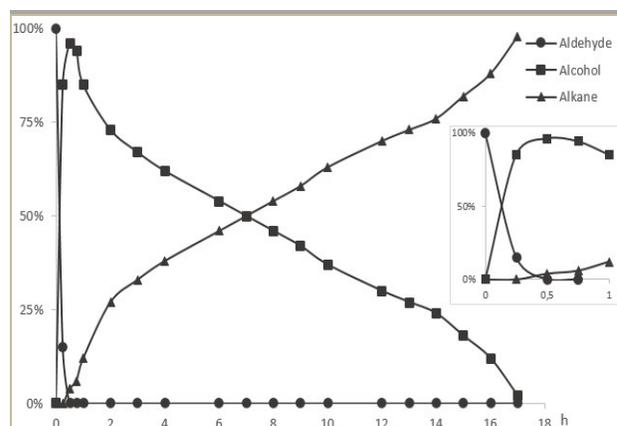
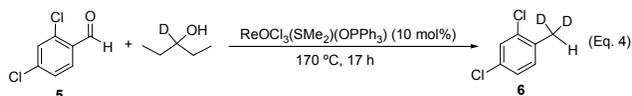


Fig. 1 Deoxygenation of 2,4-dichlorobenzaldehyde with the system 3-pentanol/ $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ (10 mol%) monitored by ^1H NMR spectroscopy.

3-pentanol/ReOCl₃(SMe₂)(OPPh₃) was monitored by ¹H NMR spectroscopy during 17 h.

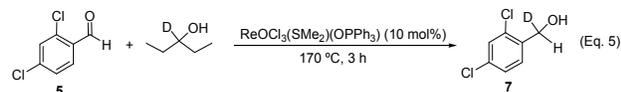
Figure 1 shows the products observed as a function of time. The analysis of the graphical indicates that the reduction of the aldehyde to the corresponding benzyl alcohol is very fast (30 min), confirming that the alcohol is an intermediate in the deoxygenation of the aldehyde. The graphical also shows that the deoxygenation of the 2,4-dichlorobenzyl alcohol is the limiting step in the direct deoxygenation of the aldehyde to the alkane, requiring nearly 16 h 30 min.

To confirm the deoxygenation of the carbonyl group by the reducing agent 3-pentanol, we carried the reaction of 2,4-dichlorobenzaldehyde with deuterated 3-pentanol (3-pentanol-D) at 170 °C (Eq. 4). However, after 17 h we observed the formation of the deuterated alkane **6** in low yield (10%).



The analysis of the ¹H NMR spectrum of the deuterated alkane **6** shows a signal at δ 2.32 ppm, integrating only one proton that confirms the incorporation of the two deuterium atoms in the alkane (Fig. 2b).

Then, we decided to follow the reduction of 2,4-dichlorobenzaldehyde with 3-pentanol-D by ¹H NMR spectroscopy and we observed the formation of the deuterated alcohol **7** after 3 h (Eq. 5). We stopped the reaction and the alcohol was isolated by column chromatography.



The ¹H NMR spectrum of deuterated alcohol **7** presents a signal at δ 4.71 ppm that integrates one proton, which is

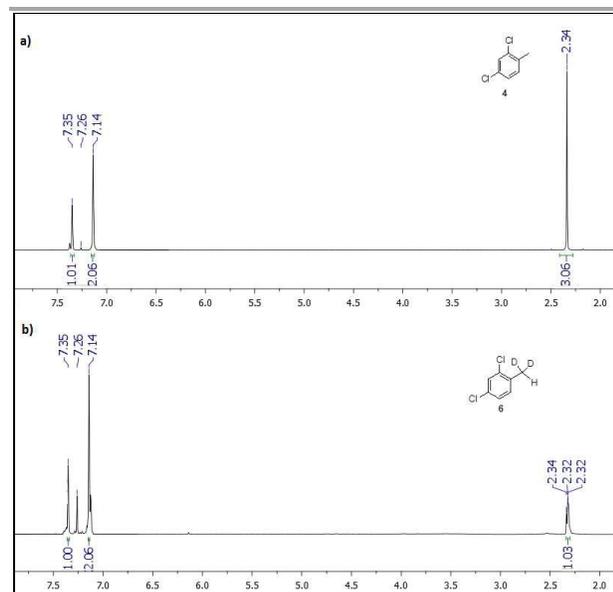


Fig. 2 ¹H NMR spectra (CDCl₃, 400 MHz) of: (a) compound **4**; (b) deuterated alkane **6**.

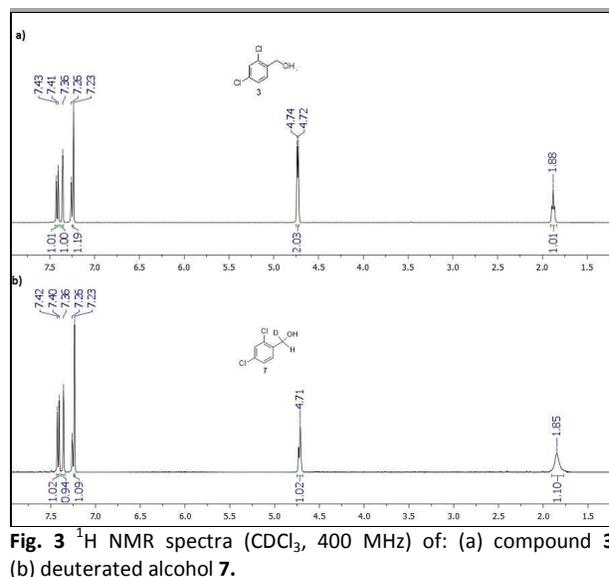


Fig. 3 ¹H NMR spectra (CDCl₃, 400 MHz) of: (a) compound **3**; (b) deuterated alcohol **7**.

consistent with the reduction of the carbonyl group with the incorporation of one deuterium atom (Figure 3b).

We also performed the reaction between the reducing agent (3-pentanol) and the catalyst ReOCl₃(SMe₂)(OPPh₃) at 170 °C during 17 h, leading to the oxidation of the 3-pentanol to 3-pentanone, confirmed by ¹H and ¹³C NMR spectroscopy (see supporting information).

Based on these results, we suggest that the deoxygenation of the carbonyl compounds with the system 3-pentanol/ReOCl₃(SMe₂)(OPPh₃) involves the oxidation of the 3-pentanol to the corresponding 3-pentanone and the hydride transfer from the 3-pentanol to the carbonyl group as confirmed by the incorporation of the deuterium atom in the alcohol **7**. Finally, occurs the deoxygenation of the alcohol by reaction with another molecule of 3-pentanol.

Comparing this novel methodology using the system 3-pentanol/ReOCl₃(SMe₂)(OPPh₃) with the other methods developed by our group for the deoxygenation of carbonyl compounds,^{28,29} we conclude that this novel procedure is more economical, environmental friendly using an alcohol as a green solvent/reducing agent instead of a silane. Furthermore, this method is also more efficient and selective for the deoxygenation of ketones to the corresponding alkenes that the method catalyzed by the same oxo-rhenium complex ReOCl₃(SMe₂)(OPPh₃) employing PhSiH₃ as reducing agent, which produced a mixture of alkane and alkene in the reaction of several substrates, being the alkene the minor product.

Conclusions

We have developed the first methodology for the deoxygenation of ketones to the corresponding alkenes and for the deoxygenation of aldehydes to alkanes using an alcohol as a green solvent/reducing agent catalyzed by the oxo-rhenium complex ReOCl₃(SMe₂)(OPPh₃) in moderate to excellent yields. This procedure has some advantages over the

other reported in the literature that use toxic hydride reagents or molecular hydrogen (H₂), its use is generally associated with high pressure, special equipment, and safety precautions to minimize the explosion risk.

This novel method is also chemoselective and the catalyst can be used in several cycles with good activity. Together, all these advantages make this catalytic protocol a green and more economic process for the deoxygenation of ketones and aldehydes. We believe that this system can be applied in the near future to the deoxygenation of carbonyl compounds in the context of biomass derived chemicals synthesis.

Experimental

General procedure for the deoxygenation of carbonyl compounds with the system 3-pentanol/ReOCl₃(SMe₂)(OPPh₃)

The solution of ReOCl₃(SMe₂)(OPPh₃) (5–10 mol%) and carbonyl compound (0.5 mmol) in 3-pentanol (2 ml) was stirred at 170 °C under air atmosphere in a closed Schlenk equipped with a J-Young tap without using any special pressure-controlling equipment (the reaction times are indicated in Tables 3 and 4 and all reaction temperatures refer to bath temperatures). The reaction mixture of the less volatile products was evaporated and purified by silica gel column chromatography with *n*-hexane. The yields of more volatile deoxygenated products were determined directly by ¹H NMR spectroscopy using 1,2-dimethoxyethane as the internal standard.

Acknowledgements

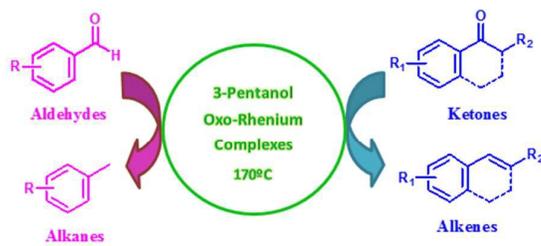
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Graphical Abstract



The catalytic system 3-pentanol/ $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ was very efficient for the deoxygenation of carbonyl compounds.