ChemPubSoc Europe

DOI: 10.1002/cctc.201500560

CHEMCATCHEM
Full Papers

Dioxomolybdenum Complexes as Excellent Catalysts for the Deoxygenation of Aryl Ketones to Aryl Alkenes

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This work describes a new methodology for the selective deoxygenation of aryl ketones to the corresponding aryl alkenes catalyzed by dioxomolybdenum complexes using silanes as reducing agents. The best results were obtained with the system $PhSiH_3/MoO_2Cl_2(H_2O)_2$ (5–10 mol %), which was very efficient for the deoxygenation of a large variety of aryl ketones to alkenes in excellent yields. This new methodology has the advantages of using an inexpensive, environmentally friendly, easily prepared, and air-stable catalyst in ether solution.

Introduction

The deoxygenation of ketones to the corresponding alkenes is a very useful chemical transformation in organic chemistry. For example, the decarbonylation of ketones from biomass resources is an important reaction because of concerns about diminishing petroleum reserves, increasing fuel prices, and minimizing environmental impact and has been a key target in chemistry and chemical engineering.[1,2] However, there are very few methods reported in the literature for the selective direct deoxygenation of ketones to alkenes. One example is the method reported by Hiegel and Carney, which is a modification of the Clemmensen reduction and uses amalgamated zinc and formic acid in ethanol under reflux.[3] The Shapiro reaction also provides a convenient method to convert ketones into a plethora of olefinic substances in high yields by the reaction of ketones with (phenylsulfonyl)hydrazine to form the corresponding hydrazones, which react with a strong base, such as *n*-butyllithium, to produce the olefins.[4]

In the last decade, high-valence oxomolybdenum complexes have proved to be excellent catalysts for the reduction of organic compounds,[5] such as aldehydes and ketones,[6] esters,[7] amides,[8] imines,[9] sulfoxides,[10] *N*-oxides,[10a,11] aromatic nitro compounds,[12] epoxides,[13] alcohols, and polyols,[14] using phosphorus compounds, silanes, boranes, H_2, and alcohols as reducing agents.

Very recently, we investigated the direct reductive deoxygenation of ketones catalyzed by high-valence oxorhenium complexes using a silane as the reducing agent.[15] The systems $PhSiH_3/ReOCl_3(SMe_2)(OPPh_3)$ (2 mmol/5 mol %) and $PhSiH_3/ReOCl_3(PPh_3)_2$ (2 mmol/5 mol %) led to the deoxygenation of aryl ketones to produce the corresponding alkanes selectively or a mixture of alkane and alkene derivatives, and the alkane was the major product.

The search for efficient, economical, environmentally friendly, and reusable catalysts for the deoxygenation of ketones to the corresponding alkenes has led us to investigate the use of high-valence oxomolybdenum complexes as catalysts for this chemical transformation. In this work, we report the first methodology for the direct deoxygenation of a large variety of aryl ketones to alkenes in good to excellent yields catalyzed by high-valence dioxomolybdenum complexes using a silane as a reducing agent. To the best of our knowledge, there are no reports of the use of high-valence oxomolybdenum complexes as catalysts for the direct deoxygenation of ketones to alkenes.

Results and Discussion

Initially, we compared the catalytic activity of several dioxomolybdenum complexes in the deoxygenation of ketones (Table 1). The reduction of deoxyanisoin with phenylsilane (2 mmol) in the presence of 5 mol % of the oxo complex $MoO_2Cl_2(H_2O)_2$ was very efficient and afforded the alkene in excellent yields (98 %) after 16 h in THF under reflux and an air atmosphere in a closed Schlenk flask equipped with a J. Young tap (Table 1, entry 1). No reduction was observed at room temperature (Table 1, entry 2). In the presence of 3 mol % of $MoO_2Cl_2(H_2O)_2$, the alkene was obtained in only 62 % yield (Table 1, entry 3). Usually, the reductions catalyzed by the dioxomolybdenum complex MoO_2Cl_2 are performed under an inert atmosphere with dry solvents. Under these reaction conditions, the deoxygenation of deoxyanisoin produced the alkene in excellent yield (93 %). This reduction was also performed under an air atmosphere in solvent that had not been dried, and the alkene was obtained in similar yield (91 %; Table 1, entry 4). The reduction of deoxyanisoin was also performed with 5 or 10 mol % of $MoO_2Cl_2(dmso)_2$. These two reductions afforded the alkene in 63 and 83 % yields, respectively (Table 1, entries 5 and 6). The dioxo complex

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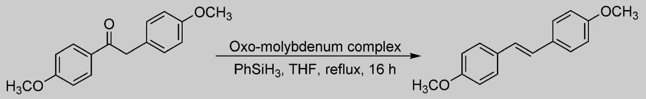
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201500560.

Table 1. Reductive deoxygenation of deoxyanisoin catalyzed by different dioxomolybdenum complexes.[a]



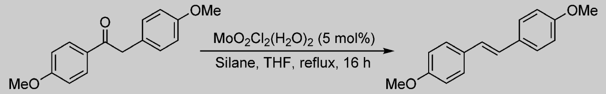
Entry	Catalyst	Catalyst [mol %]	*T*	Yield [%][b]
1	$MoO_2Cl_2(H_2O)_2$	5	reflux	98
2	$MoO_2Cl_2(H_2O)_2$	5	RT	no reaction
3	$MoO_2Cl_2(H_2O)_2$	3	reflux	62
4	MoO_2Cl_2	5	reflux	91
5	$MoO_2Cl_2(dmso)_2$	5	reflux	63
6	$MoO_2Cl_2(dmso)_2$	10	reflux	83
7	$MoO_2Cl_2[(4\text{-}ClPh)_2SO]_2$	5	reflux	63
8	$MoO_2Cl_2[(4\text{-}ClPh)_2SO]_2$	10	reflux	73
9	$MoO_2Cl_2(OPPh_3)_2$	10	reflux	35 (21)[c,d]
10	$MoO_2(acac)_2$	10	reflux	16 (83)[e]
11	$MoO_2Cl_2(dmf)_2$	10	reflux	3 (6)[f] (93)[e]
12	$MoO_2Cl_2(bipy)$	10	reflux	no reaction
13	without catalyst	–	reflux	no reaction

[a] The reactions were performed with 1.0 mmol of deoxyanisoin and 2.0 mmol of $PhSiH_3$. [b] Isolated yields. [c] Yield of alkane. [d] Yield of alkene/alkane determined by ^1H NMR spectroscopy. [e] Substrate recovered. [f] Yield of alcohol.

$MoO_2Cl_2[(4\text{-}ClPh)_2SO]_2$ (5–10 mol %) was also tested in the reduction of deoxyanisoin and produced the alkene in moderate yields (63–73 %; Table 1, entries 7 and 8). In contrast, low yields of alkene were obtained in the reductions catalyzed by the oxo complexes $MoO_2Cl_2(OPPh_3)_2$, $MoO_2(acac)_2$ (acac = acetylacetonate), and $MoO_2Cl_2(dmf)_2$ (Table 1, entries 9–11). In the reaction performed in the presence of $MoO_2(OPPh_3)_2$, we also observed the formation of the corresponding alkane in 21 % yield (Table 1, entry 9). Finally, no reaction occurred in the presence of the 2,2′-bipyridine-derived complex $MoO_2Cl_2(bipy)$ (Table 1, entry 12) or in the absence of catalyst (Table 1, entry 13).

The reduction of deoxyanisoin was also investigated with several silanes. Phenylsilane (2 mmol) was the best reducing agent, which produced the alkene in 98 % yield in THF under reflux after 16 h (Table 2, entry 1). If only 1 mmol of $PhSiH_3$ was used, the reaction was incomplete and afforded 59 % yield of alkene (Table 2, entry 2). A good yield of alkene (83 %) was observed in the reaction performed with polymethylhydrosiloxane (PMHS; Table 2, entry 3). In contrast, the reductions performed with the silanes $PhMe_2SiH$, Et_3SiH, and Pr_3SiH gave low yields of alkene (Table 2, entries 4–6). No reaction was observed if Ph_3SiH was used or in the absence of silane (Table 2, entries 7 and 8).

Table 2. Reductive deoxygenation of deoxyanisoin catalyzed by $MoO_2Cl_2(H_2O)_2$ using different silanes.[a]



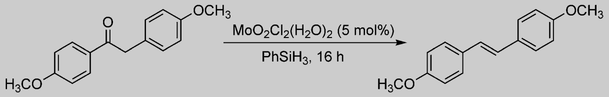
Entry	Silane	Silane [mmol]	Yield [%][b]
1	$PhSiH_3$	2.0	98
2	$PhSiH_3$	1.0	59 (13)[c]
3	PMHS	2.0	83 (5)[c]
4	$PhMe_2SiH$	2.0	39 (45)[c]
5	Et_3SiH	2.0	20 (80)[c]
6	Pr_3SiH	2.0	25 (75)[c]
7	Ph_3SiH	2.0	no reaction
8	without silane	–	no reaction

[a] The reactions were performed with 1.0 mmol of deoxyanisoin. [b] Isolated yields. [c] Substrate recovered.

The reduction of deoxyanisoin was also performed in different solvents to evaluate their effect (Table 3). THF was the best solvent for this reaction at reflux temperature and afforded the alkene in 98 % yield (Table 3, entry 1). However, this reduction does not occur at room temperature (Table 3, entry 2). Diethyl ether and benzene gave good to moderate yields of alkene (Table 3, entries 3 and 4). Finally, the reactions performed in dioxane, toluene, dichloromethane, chloroform, and acetonitrile only afforded low yields of the alkene (Table 3, entries 5–9).

We decided to explore the reduction of several aryl ketones with the system $PhSiH_3/MoO_2Cl_2(H_2O)_2$ (5–10 mol %) in THF under reflux in a closed Schlenk flask equipped with a J. Young tap under an air atmosphere to evaluate the scope and limitations of this system. The yields of less volatile alkenes were determined after purification by silica gel column chromatography, and the yields of the more volatile products were determined directly by ^1H NMR spectroscopy using 1,2-dimethoxyethane as the internal standard.

Table 3. Reductive deoxygenation of deoxyanisoin in different solvents.[a]

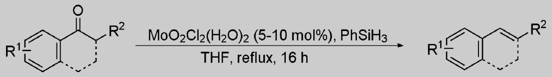


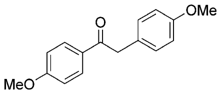
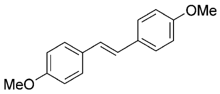
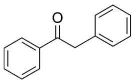
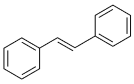
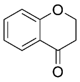
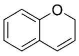
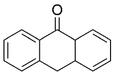
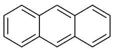
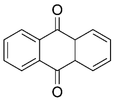
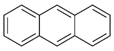
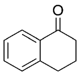
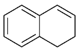
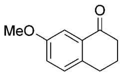
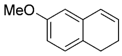
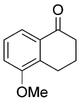
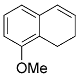
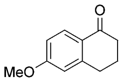
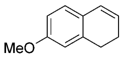
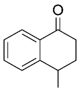
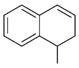
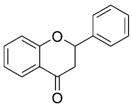
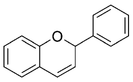
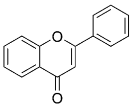
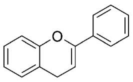
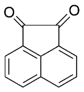
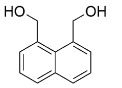
Entry	Solvent	*T*	Yield [%][b]
1	THF	reflux	98
2	THF	RT	no reaction
3	Et_2O	reflux	71 (8)[c,d]
4	benzene	reflux	54 (15)[c,d]
5	dioxane	reflux	48
6	toluene	reflux	32 (12)[c,d]
7	CH_2Cl_2	reflux	30 (5)[e] (35)[f]
8	$CHCl_3$	reflux	20 (5)[e] (40)[f]
9	MeCN	reflux	6 (94)[f]

[a] The reactions were performed with 1.0 mmol of deoxyanisoin and 2.0 mmol of $PhSiH_3$. [b] Isolated yields. [c] Yield of alkane. [d] Yield alkene/alkane determined by ^1H NMR spectroscopy. [e] Yield of alcohol. [f] Substrate recovered.

The best result was obtained in the reduction of deoxyanisoin catalyzed by 5 mol % of $MoO_2Cl_2(H_2O)_2$, which produced the alkene in the *trans* configuration selectively in 98 % yield after purification by silica gel column chromatography (Table 4, entry 1). The deoxygenation of the substrate deoxybenzoin led to a decrease in the yield of the corresponding alkene (83 %)

Table 4. Reductive deoxygenation of aryl ketones with the $PhSiH_3/MoO_2Cl_2(H_2O)_2$ system.[a]



Entry	Ketone	Product	$MoO_2Cl_2(H_2O)_2$ [mol %]	Yield [%][b]
1			5	98
2			10	83 (5)[c]
3			10	90
4			10	87
5			10	57[d] (31)[c]
6			10	90[e]
7			10	84[e]
8			10	78[e]
9			10	70 (14)[e,f]
10			10	80[e]
11			10	54 (44)[c]
12			10	80 (10)[d]
13			10	77

[a] The reactions were performed with 1.0 mmol of ketone, 5–10 mol% of $MoO_2Cl_2(H_2O)_2$, and 2.0–4.0 mmol of $PhSiH_3$. [b] Isolated yields. [c] Substrate recovered. [d] Yield of alcohol. [e] Yield of the reaction determined by ^1H NMR spectroscopy. [f] Yield of alkane.

even if we used a higher amount of catalyst (10 mol%) (Table 4, entry 2). In this reaction the *trans* isomer was also obtained selectively.

The reduction of 4-chromanone with the $PhSiH_3/MoO_2Cl_2(H_2O)_2$ (10 mol%) system produced 90% yield of alkene (Table 4, entry 3), and the deoxygenation of anthrone led to the formation of anthracene in 87% yield (Table 4, entry 4). The anthracene was also isolated in moderate yield from the deoxygenation of the two carbonyl groups of anthraquinone by using 4.0 mmol of $PhSiH_3$ (Table 4, entry 5).

This methodology was also explored in the deoxygenation of several tetralones. The best result was observed in the reduction of α-tetralone, which produced the corresponding alkene in 90% yield (Table 4, entry 6). The deoxygenation of 5-, 6-, and 7-methoxytetralone also gave good yields of the alkenes (70–84%; Table 4, entries 7–9). In the reduction of 6-methoxytetralone, we also observed the formation of 14% yield of alkane (Table 4, entry 9). Finally, the reaction of 4-methyltetralone afforded the corresponding alkene in 80% yield (Table 4, entry 10).

The deoxygenation of the natural product flavanone with the $PhSiH_3/MoO_2Cl_2(H_2O)_2$ (10 mol%) system produced the alkene in 54% yield (Table 4, entry 11). In contrast, a very interesting result was obtained in the reaction of another natural product the flavone, which allowed the conversion of the carbonyl group into the methylene group in 80% yield along with the formation of the corresponding alcohol in 10% yield (Table 4, entry 12). Finally, the reduction of acenaphthenequinone produced 1,8-naphthalenedimethanol in 77% yield by using 4.0 mmol of $PhSiH_3$ (Table 4, entry 13).

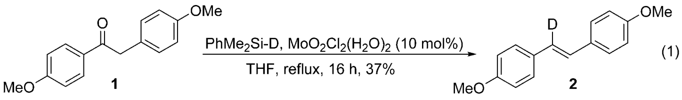
In contrast, this system was not efficient for the deoxygenation of cyclohexanone and β-tetralone.

We also observed that the dioxomolybdenum complex $MoO_2Cl_2(H_2O)_2$ could be used in more than one catalytic cycle. We performed successive reactions by the sequential addition of fresh α-tetralone and phenylsilane to the reaction mixture. The results obtained showed that $MoO_2Cl_2(H_2O)_2$ can be used in two catalytic cycles to achieve the same activity (90%). However, the deoxygenation of this substrate was not completed in the third cycle (52%).

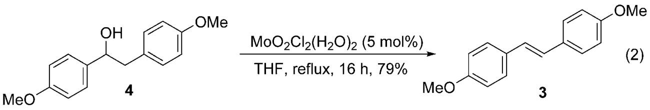
This new methodology has the advantage of using the air-stable oxo complex $MoO_2Cl_2(H_2O)_2$ as the catalyst, which has an easy and inexpensive preparation by extraction from a hydrochloric acid solution of Na_2MoO_4 with diethyl ether.[16]

We propose that the mechanism for the deoxygenation of the aryl ketones to the corresponding alkenes with the catalytic system of $PhSiH_3/MoO_2Cl_2(H_2O)_2$ involves the formation of a hydride species, which results from Si–H bond activation of the silane by the oxo molybdenum complex as demonstrated in our previous work,[17] followed by the reduction of the ketone to the corresponding alcohol. If phenylsilane is used as the reducing agent, the major product obtained in the reduction of the ketone is the alcohol and not the silyl ether, probably because of the instability of the silyl ether formed from this silane. Finally, the dehydration of the alcohol to the alkene occurs.

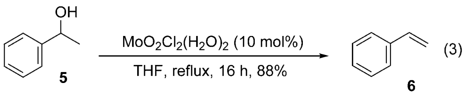
Several experiments were performed to support this mechanism. The reduction of deoxyanisoin was performed using deuterated dimethylphenylsilane ($PhMe_2Si$-D) catalyzed by $MoO_2Cl_2(H_2O)_2$ (10 mol%) in THF under reflux [Eq. (1)]. After purification, the deuterated alkene **2** was isolated in 37% yield [Eq. (1)]. The ^{1}H NMR spectrum of this compound shows a singlet at $\delta = 6.93$ ppm, which integrates only one proton (Supporting Information) and confirms the incorporation of deuterium in **2**. In contrast, the singlet at $\delta = 6.93$ ppm in the ^{1}H NMR spectrum of alkene **3** obtained in the reaction with $PhMe_2SiH$ integrates two protons (Supporting Information).

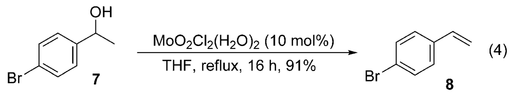


We also investigated the deoxygenation of the alcohol **4** in the presence of $MoO_2Cl_2(H_2O)_2$ in THF under reflux without the addition of the reducing agent to obtain the alkene **3** in 79% yield [Eq. (2)]. This result shows that the oxomolybdenum complex promotes the dehydration of the alcohol to the corresponding alkene [Eq. (2)].



Then, we explored the catalytic activity of $MoO_2Cl_2(H_2O)_2$ in the dehydration of the alcohols **5** and **7** without the addition of any reducing agent, which afforded the corresponding styrene in 88% yield and 4-bromostyrene in 73% yield, determined by ^{1}H NMR spectroscopy using 1,2-dimethoxyethane as the internal standard [Eqs. (3) and (4)]. In contrast, no reaction was observed in the deoxygenation of the primary alcohol 2-phenylethanol. The results obtained demonstrated that $MoO_2Cl_2(H_2O)_2$ catalyzes the dehydration of secondary alcohols. We believe that the deoxygenation of alcohols catalyzed by $MoO_2Cl_2(H_2O)_2$ involves the coordination of the alcohol to Mo with the release of a ligand and the transfer of two hydrogen atoms, which results in the formation of the alkene and a molecule of water. Gebbink and co-workers have also reported the deoxygenation of alcohols to the corresponding alkenes using several $MoO_2(acac')_2$ complexes as catalysts without the addition of a reducing agent, but the yields of the alkenes obtained are, in general, low.[18]





Conclusions

We have developed a new and efficient method for the direct and selective deoxygenation of aryl ketones to the corresponding aryl alkenes with the $PhSiH_3/MoO_2Cl_2(H_2O)_2$ (5–10 mol%) system. This is the first methodology for the deoxygenation of carbonyl compounds catalyzed by oxomolybdenum complexes, and the results obtained extend the scope of the use of high-valence oxomolybdenum complexes as efficient catalysts for the deoxygenation of ketones.

If we compare this methodology with our procedure for the deoxygenation of aryl ketones with the silane/oxorhenium complex system,[14] this new method is more selective for the deoxygenation of ketones to alkenes in excellent yields. In contrast, our previous method produced an inseparable mixture of alkane and alkene with a low yield of alkene in the reaction of several substrates. The use of oxomolybdenum complexes for the deoxygenation of ketones instead of oxorhenium complexes makes the deoxygenation of ketones more economic and less toxic.

This new method has the following advantages: (1) excellent catalytic activity; (2) easy and inexpensive preparation of the catalyst; (3) the use of an environmentally friendly catalyst; (4) $MoO_2Cl_2(H_2O)_2$ is air stable in ether solution; (5) applicability to a large variety of ketones; (6) the reactions can be performed under an air atmosphere without using dry solvents; (7) the catalyst can be used in more than one catalytic cycle.

The formation of the methylene group in the reduction of the flavone (Table 4, entry 12) suggests that the $PhSiH_3/MoO_2Cl_2(H_2O)_2$ system can also be applied to the direct reductive deoxygenation of ketones to the corresponding alkanes.

The dehydration of alcohols **4**, **5**, and **7** to the alkenes catalyzed by $MoO_2Cl_2(H_2O)_2$ in good yields without a reducing agent suggests that this catalyst can be an excellent, inexpensive, easily available, and environmentally friendly alternative to the oxorhenium complexes reported recently[19] for the deoxygenation of alcohols and polyols, which is a very useful reaction to deoxygenate biomass resources.

Further mechanistic studies, which include computational studies, and new applications of this method with other oxo complexes, reducing agents, and substrates are under investigation in our group.

Experimental Section

Deoxygenation of aryl ketones to the corresponding alkenes with the $PhSiH_3/MoO_2Cl_2(H_2O)_2$ system

To a solution of $MoO_2Cl_2(H_2O)_2$ (5–10 mol%) and ketone (1.0 mmol) in THF (3 mL) was added $PhSiH_3$ (2.0–4.0 mmol). The reaction mixture was stirred under reflux under an air atmosphere in a closed

Schlenk flask equipped with a J. Young tap for 16 h. The reaction mixture of the less volatile products was evaporated and purified by silica gel column chromatography with *n*-hexane to afford the corresponding alkenes. The yields of more volatile deoxygenated products were determined directly by ^{1}H NMR spectroscopy using 1,2-dimethoxyethane as the internal standard.

Dehydration of alcohols to the corresponding alkenes catalyzed by $MoO_2Cl_2(H_2O)_2$ without reducing agent

The solution of $MoO_2Cl_2(H_2O)_2$ (5–10 mol%) and alcohol (1.0 mmol) in THF (3 mL) was stirred under reflux under an air atmosphere in a closed Schlenk flask equipped with a J. Young tap for 16 h. The reaction mixture of the less volatile alkenes was evaporated and purified by silica gel column chromatography with *n*-hexane to afford the alkenes. The yields of the more volatile alkenes were determined directly by ^{1}H NMR spectroscopy using 1,2-dimethoxyethane as the internal standard.

Acknowledgements

This research was supported by the Fundação para a Ciência e Tecnologia (FCT) through project PTDC/QUI-QUI/110080/2009. T.A.F. thanks the FCT for a grant. The authors thank the project UID/QUI/00100/2013 and the Portuguese NMR Network (IST-UTL Center) for providing access to the NMR facilities.

Keywords: alkenes · ketones · molybdenum · reduction · silanes

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Received: May 19, 2015