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Pinacol as a New Green Reducing Agent: Molybdenum-Catalyzed Chemoselective Reduction of Sulfoxides and Nitroaromatics

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Abstract. Pinacol is described as a new chemoselective and environmentally benign reducing agent for sulfoxides and nitroaromatics assisted by readily available dichlorodioxomolybdenum(VI) complexes as catalysts. A wide range of substrates including those bearing challenging functional groups have been efficiently and selectively reduced being acetone and water the only by-products of these reactions.

Keywords: chemoselectivity; molybdenum; nitro compounds; reduction; sulfoxides

The development of new synthetic technologies for the reduction of oxygenated compounds that are more economical and environmentally friendly than traditional methods based on the use of precious metals as catalysts and/or the employment of hazardous/toxic reagents is a key target in both industry and academic laboratories. Despite many achievements have been got in this area, the search for milder, selective, and catalytic procedures where the presence of sensitive and/or reducible substituents can be tolerated remains as an important goal in organic synthesis.[1]

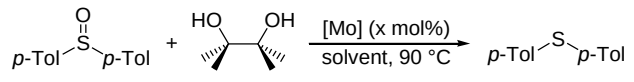
In this field, the deoxygenation of sulfoxides is important from both synthetic and biological points of view. Due to the high potential of sulfoxides as intermediates in a variety of synthetic transformations, mainly as chiral auxiliaries, there is a continuous interest in the development of novel methods for their deoxygenation to the corresponding sulfides,[2] as this is usually the first step for their further removal. Moreover, the selective reduction of aromatic nitro compounds,[3] that encompass hydrogenation,[4] electron-transfer[5] and hydride-transfer[6] reactions, is the principal method for accessing anilines. Among all of these strategies, the catalytic hydrogenation has experienced a significant development. However, the lack of chemoselectivity in the reduction of nitroarenes containing functional groups such as olefins, nitriles or halides,[7] as well as the handle of H_2 limits the applicability of these procedures. Alternatively, reactions involving other reducing agents such as silanes,[8] or different hydrogen transfer sources,[9] usually require an excess of these reagents and produce toxic by-products sometimes difficult to remove from the reaction media. Moreover, catalysts derived from expensive metals are frequently needed for all these processes. Therefore, the development of novel green catalytic methodologies for the reduction of both nitroarenes and sulfoxides that exhibit broad tolerance to functionality remains an actual challenge.

On the other hand, dioxomolybdenum(VI) complexes with the *cis*-$[MoO_2]^{2+}$ core, and in particular addition compounds of dichlorodioxomolybdenum(VI), are relatively non-toxic and inexpensive compounds that are able to catalyze a variety of oxygen atom transfer reactions.[10] In this field we have reported the first examples of the Mo-catalyzed deoxygenation of sulfoxides[11] and *N*-oxides,[12] as well as the reductive cyclization of nitroaromatics.[13] In those processes phosphorous(III)-based reagents were used as oxygen-acceptors. Later on, other authors have also reported similar dioxomolybdenum(VI)-catalyzed reactions using alternative reductants such as silanes,[14] boranes,[15] and hydrogen.[16] In this context, we became interested in the search for new reagents that could act as oxygen-acceptors in this type of Mo-catalyzed reductions, in order to develop cleaner processes with easily removed by-products as well as to avoid the handling of H_2 or hazardous reagents. Taking into account a recent report in which pinacol (2,3-dimethyl-2,3-butanediol) was able to reduce an oxovanadium(V) dipicolinate complex to a vanadium(III) μ-oxo dimmer,[17] we reasoned that this diol could also reduce dioxomolybenum(VI) complexes to oxomolybdenum(IV) ones, thus opening the possibility of using it as a new reducing agent. Herein we report the use of pinacol as reducing agent in Mo-catalyzed reduction reactions of

sulfoxides and nitroarenes. These reactions, that generate acetone and water as the only by-products, occur in high yields and show broad scope including substrates bearing potentially reducible functional groups.

Based on our previous method for the deoxygenation of sulfoxides with phosphites,[11] an initial experiment was carried out with bis(*p*-tolyl)sulfoxide **1a** as model substrate in MeCN at reflux using $MoO_2Cl_2(dmf)_2$ as catalyst and 2 equiv of pinacol as oxygen-acceptor (Table 1, entry 1). Gratifyingly, complete conversion was observed after 4 h and the corresponding sulfide **2a** was isolated in 85% yield. Using commercially available MoO_2Cl_2 the reaction was slower (entry 2).[18] As expected, no appreciable reaction took place without catalyst (entry 3). Reactions conducted in toluene or DME also occurred to full conversion and good yield in 2-5 h (entries 4−5), whereas low conversion was observed by performing the reduction in water (entry 6). Interestingly, reaction under solvent-free conditions afforded the highest yield of the thioether **2a** in the shortest reaction time (entry 7). Further tests lowering the reaction temperature (entry 8), the catalyst loading (entries 9−10) or the amount of pinacol (entry 11) proved that the reduction could be performed to full conversion under milder conditions although inferior results in terms of reaction time and yield were observed.

Table 1. Optimization of the reaction conditions for the reduction of sulfoxide **1a**.



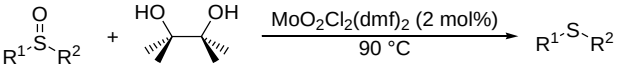
1a n equiv **2a**

Entr.	[Mo]	mol %	Solvent	Pinacol equiv	*t* [h]	Yield [%][a]
1	$MoO_2Cl_2(dmf)_2$	2	MeCN	2	4	85 (100)
2	MoO_2Cl_2	2	MeCN	2	7	84 (100)
3	–	–	MeCN	2	48	– (0)
4	$MoO_2Cl_2(dmf)_2$	2	toluene	2	2	78 (100)
5	$MoO_2Cl_2(dmf)_2$	2	DME	2	3	81 (100)
6	$MoO_2Cl_2(dmf)_2$	2	H_2O	2	24	– (18)
7	$MoO_2Cl_2(dmf)_2$	2	–	2	2	91 (100)
8	$MoO_2Cl_2(dmf)_2$	2	–	2	14	76 (100)
9	$MoO_2Cl_2(dmf)_2$	1	–	2	8	78 (100)
10	$MoO_2Cl_2(dmf)_2$	0.5	–	2	72	71 (100)
11	$MoO_2Cl_2(dmf)_2$	2	–	1	5	78 (100)

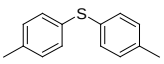
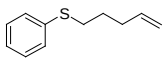
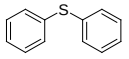
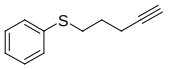
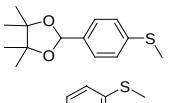
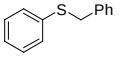
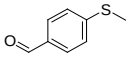
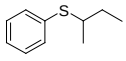
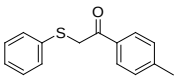
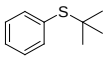
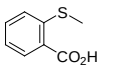
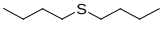
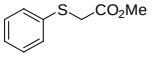
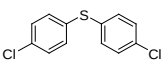
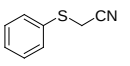
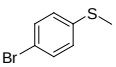
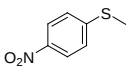
[a] Based on the starting sulfoxide **1a**; in brackets conversion estimated by ^{1}H NMR (300 MHz) from the crude reaction mixture. [b] Reaction conducted at 70 °C.

Using the optimal conditions, i.e. 2 equiv of pinacol and $MoO_2Cl_2(dmf)_2$ (2 mol%) at 90 ºC without any solvent, the deoxygenation of selected sulfoxides **1** was examined. A variety of diaryl-, alkylaryl-, and dialkyl sulfoxides gave rise to high yields of the corresponding sulfides (Table 2, entries 1−14). Interestingly, this method can be applied to multigram synthesis as 9.4 g of **2a** (90% isolated yield) were easily prepared in one batch from 11.5 g (50 mmol) of **1a** (entry 2). Moreover, we have developed an alternative protocol under microwave irradiation that shortens the required time for the reduction from 2-4 h to 5-10 minutes, obtaining the final sulfides in similar yields to those obtained by conventional heating (entries 3,5,7,10,12,14 and 16). In addition, sulfoxides bearing potentially reducible substituents such as halogens, C–C multiple bonds, keto or cyano groups were chemoselectively reduced to the corresponding thioethers without affecting the additional functionality (entries 15–26). In the case of 4-methanesulfinylbenzaldehyde, simultaneous acetalization of the carbonyl group takes place (entry 20). However, a simple acidic workup of the reaction mixture allowed the synthesis of 4-methylsulfanylbenzaldehyde (entry 21). Finally, reaction of methyl 4-nitrophenyl sulfoxide produced a small amount (ca. 7%) of 4-aminophenyl methyl sulfide as byproduct, as a result of the simultaneous reduction of the nitro group (entry 27). Nevertheless, the selective reduction of the sulfoxide was achieved performing the reaction with 1 equiv of pinacol (entry 28).

Table 2. Deoxygenation of sulfoxides **1**.

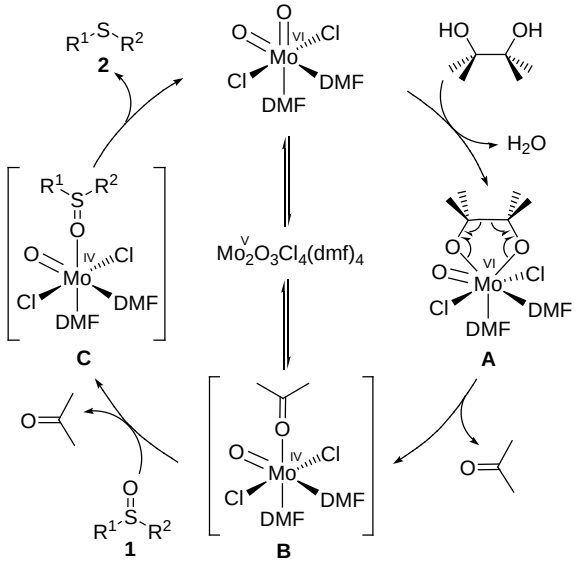


1 (2 equiv) **2**

Entr.	Product	Yield [%][a]	Entr.	Product	Yield [%][a]
1		91			
2[b]		90	18		82
3[c]		98			
4		89			
5[c]		85	19		91
6		92			
7[c]		92	20		89
8		91	21[e]		88
9		90	22		78
10[c]		89			
11		89	23[d]		90
12[c]		87	24[f]		85
13		79	25		79
14[c]		93			
15[d]		99	26		83
16[c]		91			
17		91	27[f]		80[g]
			28[f,h]		86

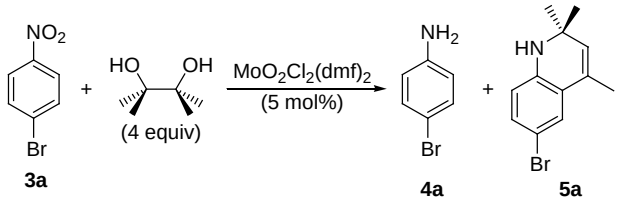
[a] Based on the starting sulfoxide **1**. [b] 50 mmol scale. [c] Reaction conducted under MW irradiation (120 ºC, 300 W); see Supporting Information for details. [d] Reaction performed using 4 equiv of pinacol. [e] HCl and THF were added to the crude mixture and it was stirred under reflux. [f] Reaction conducted in MeCN. [g] Partial reduction (ca 7%) to 4-aminophenyl methyl sulfide was observed. [h] Reaction conducted with 1 equiv of pinacol.

The catalytic cycle involved in the reduction could be represented as shown in Scheme 1. $MoO_2Cl_2(dmf)_2$ reacts with pinacol leading to water and the pinacolate complex $MoO(pinacolate)Cl_2(dmf)_2$ (**A**). We propose the formation of this transient species based on the well documented condensation of water under mild conditions from one of the oxo ligands on dioxomolybdenum(VI) complexes and two hydrogen atoms on a number of protic compounds.[19] Oxidation of the pinacolate ligand by the molybdenum(VI) center gives rise to the oxomolybdenum(IV) species, $MoOCl_2(dmf)_2(Me_2CO)$ (**B**),[20] bearing a weakly coordinated molecule of acetone that is immediately displaced by the sulfoxide in solution to give the unstable $MoOCl_2(dmf)_2(R^1SOR^2)$ adduct (**C**), which in turn regenerates the catalyst releasing the sulfide. To support our proposal, we treated our catalyst, $MoO_2Cl_2(dmf)_2$, with pinacol in a molar ratio 1:1.2 in MeCN and, while unable to fully characterize any oxomolybdenum(IV) species, we could isolate in high yield the dinuclear oxomolybdenum(V) complex $Mo_2O_3Cl_4(dmf)_4$,[21] which displayed similar catalytic activity to that of $MoO_2Cl_2(dmf)_2$.[22] This result could be explained as it is known that oxomolybdenum(IV) complexes, formed via oxo-abstraction, present a strong tendency to comproportionate with the parent dioxomolybdenum(VI) species, and that this process is only inhibited by the presence of bulky ligands that prevent the formation of the dinuclear species.[23]



Scheme 1. Proposed catalytic cycle for the deoxygenation of sulfoxides with pinacol.

Taking into account the partial reduction of the nitro group observed with methyl 4-nitrophenyl sulfoxide (Table 2, entry 27), and considering that nitroarenes are the main precursors of functionalized anilines and have a very important role in organic synthesis, we decided to tackle the reduction of nitroaromatic compounds by using pinacol as reducing agent. Optimization of this reaction was performed on 4-bromonitrobenzene **3a**. We initially choose the optimum reaction conditions found for the deoxygenation of sulfoxides although in this case 4 equiv of pinacol and 5 mol% of catalyst were required in order to get full conversion. Under these neat conditions the expected 4-bromoaniline **4a** was obtained along with the dihydroquinoline derivative **5a**, formed by further condensation of **4a** with 2 equiv of acetone (Scheme 2).[24] Then, we studied the effect of the solvent and, gratifyingly, the formation of this side-product **5a** could be avoided by the use of *o*-xylene as solvent under reflux (method A).[25] Moreover, by applying microwave irradiation in toluene (150 ºC, 300 W) (method B) the reduction process was completed in 15 min allowing the isolation of **4a** in 95% yield (Scheme 2).



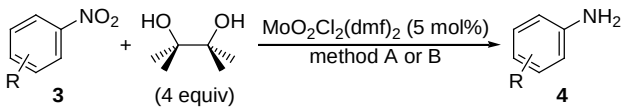
	4a	5a
no solvent, 110 °C, 48 h	73%	15%
o-xylene, 130 °C (method A), 8 h	94%	–
toluene, 150 °C, MW (method B), 15 min	95%	–

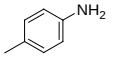
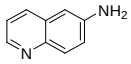
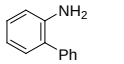
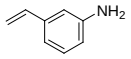
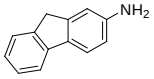
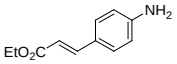
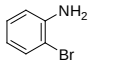
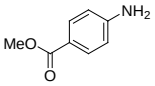
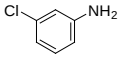
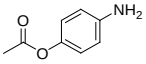
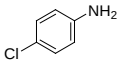
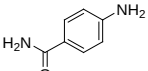
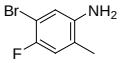
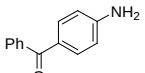
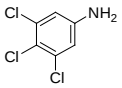
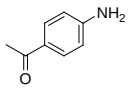
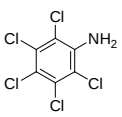
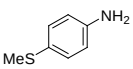
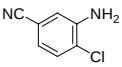
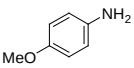
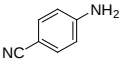
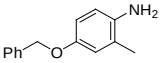
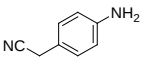
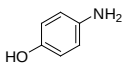
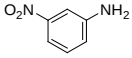
Scheme 2. Reduction of 4-bromonitrobenzene **3a** using pinacol as deoxygenating agent.

The chemoselectivity of the new developed reduction process was then explored (using either method A or B) in a selection of representative functionalized nitroarenes, including several particularly challenging substrates; the results are summarized in Table 3. Thus, reactions of nitroarenes bearing non-functionalized alkyl or aryl groups took place efficiently (Table 3, entries 1–6) even at multigram scale (entry 3). Interestingly, the present protocol, involving pinacol as reductant, allowed the selective reduction of 2-nitrobiphenyl to 2-aminobiphenyl (entries 4–5), whereas the corresponding reaction with the same dioxomolybdenum(VI) catalyst in the presence of triphenylphosphine as oxygen-acceptor exclusively afforded carbazole.[13] This result shows that under the pinacol-Mo^{VI} catalytic system nitroso intermediates are probably not generated in significant amounts. The synthesis of anilines containing halides occurred in high yields regardless of their substitution pattern (Scheme 2 and Table 3, entries 7–16).[26] In all reductions, including those of polychlorinated nitrobenzenes, no traces of dehalogenated anilines have been observed. Cyano-substituted nitrobenzenes were also selectively reduced to the corresponding cyanoanilines in high yields (entries 15–18). The methodology tolerates as well the presence of heterocycles as we have demonstrated with the preparation of 3-amino-2-chloropiridine and 6-aminoquinoline (entries 19–20). More importantly, reduction of the nitro group is also

chemoselective in the presence of olefinic bonds and, therefore, 3-nitrostyrene and ethyl *p*-nitrocinnamate led to the corresponding anilines in excellent yields and without reduction of the double bonds (entries, 21–22). Likewise, reactions of nitroarenes possessing carbonyl groups such as ester, amide or ketone occurred in high yield to exclusively afford the corresponding functionalized anilines (entries 23–28). In addition, oxygen- and sulfur-substituents, including a sensible benzyloxy group, can be present at the aromatic ring of the starting nitroarene without affecting the reduction of the nitro group (entries 29–32). Finally, using the present methodology the selective monoreduction of 1,3-dinitrobenzene to 3-nitroaniline was also achieved (entry 33). Moreover, it is also noteworthy that in most of these reductions of nitroarenes as well as in all the reactions of sulfoxides performed with our developed method, the corresponding aniline or sulfide was isolated by a simple extraction to remove the catalyst, the remaining pinacol and the water and acetone generated as by-products.

Table 3. Deoxygenation of aromatic nitro compounds **3**.[a]



Entr.	Product	Yield [%][b]	Entr.	Product	Yield [%][b]
1		95[c]			
2[d]		93	20		89
3[d,e]		85			
4		92	21		92
5[d]		90			
6		96	22		94
7		81[c]	23		82
8[d]		87[c]			
9		86[c]	24[d]		71
10		95	25[d]		88
11		89	26		93
12[d]		95	27[d]		85
13		98	28		81
14		90	29		95
15		85[c]	30		83
16[d]		87			
17		83	31		81
18		91	32[d]		78
19		85	33		75

[a] Reactions were conducted using method B (toluene, MW, 150 ºC), unless otherwise stated, requiring 15–45 min to complete. [b] Based on the starting nitroarene **3**. [c] Traces (<5%) of the corresponding dihydroquinoline **5** were also detected. [d] Reaction performed by method A (*o*-xylene, 130 ºC). [e] 50 mmol scale.

In summary, we have described the use of pinacol as a new green reducing agent for the reduction of sulfoxides and nitroarenes catalyzed by a dichlorodioxomolybdenum(VI) complex. The high selectivity of this catalytic system has been demonstrated by the chemoselective reduction of challenging substrates bearing C=C, C≡C, C=O, C≡N, halides, and OH groups. Remarkable advantages of this methodology include high isolated yields, clean reactions, easy purification, as well as availability and stability of the inexpensive catalyst. In addition, reactions can be performed in air, without any solvent in the case of sulfoxides, and under microwave heating that can dramatically shorten reaction times.

Experimental Section

General Remarks

All reactions were carried out under air atmosphere unless otherwise noted. All reaction temperatures refer to bath temperatures. All common reagents and solvents were obtained from commercial suppliers (Acros, Alfa and Aldrich) and used without further purificacion. $Na_2Mo_4{\cdot}2H_2O$ to prepare the catalyst was obtained from Acros Organics. Freshly opened commercially available (Aldrich) pinacol was used. Alternatively, pinacol is dried by azeotropic distillation and stored under N_2. Solvents were dried by standard methods. For the preparation of non commercially available sulfoxides see the Supporting Information. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-Plus 300 or Varian Inova 400 spectrometers, using $CDCl_3$, DMSO-d_6, or acetone-d_6 as solvents and internal standards. GC-MS and low resolution mass spectra (LRMS) were recorded on an Agilent 6890N/5973 Network GC System, equipped with a HP-5MS column. High resolution mass spectra (HRMS) were recorded on a Micromass AutoSpect spectrometer using EI at 70 eV. Products that had been reported previously were isolated in greater than 95% purity, as determined by ^{1}H NMR spectroscopy and capillary gas chromatography (GC). The microwave heating was performed in a microwave reactor (CEM Discover S-Class) with a single-mode microwave cavity producing continuous irradiation (Temperature measurements were conducted using an IR sensor located below the microwave cavity floor, and reaction times refer to the total hold time at the indicated temperature. The maximum wattage supplied was 300 W).

$MoO_2Cl_2(dmf)_2$

The catalyst is prepared in almost quantitative yield from commercially available $Na_2MoO_4{\cdot}2H_2O$ as previously described.[11]

General Procedure for Deoxygenation of Sulfoxides 1 with Pinacol Catalyzed by $MoO_2Cl_2(dmf)_2$

A mixture of the corresponding sulfoxide **1** (2 mmol), pinacol (472 mg, 4 mmol), and $MoO_2Cl_2(dmf)_2$ (14 mg, 0.04 mmol) was stirred at 90 °C until the sulfoxide was consumed (method A), as determined by GC-MS or TLC, or irradiated in a 10 mL sealed tube in the microwave cavity at 120 °C for 5–10 min (method B). The reaction was cooled to rt and the crude mixture was treated with 0.5 M NaOH (25 mL) and extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, and the solvents were evaporated under reduced pressure. The corresponding sulphide **2** was obtained in pure form without further purification in the yields reported in Table 2. Characterization data and NMR spectra are presented in the Supporting Information.

General Procedure for the Reduction of Nitro Compounds 3 with Pinacol Catalyzed by $MoO_2Cl_2(dmf)_2$

A mixture of the corresponding nitroaromatic derivative **3** (1 mmol), pinacol (472 mg, 4 mmol), and $MoO_2Cl_2(dmf)_2$ (17 mg, 0.05 mmol) in dry *o*-xylene (2 mL) or toluene (2 mL) was stirred at 130 °C (method A) or irradiated in a 10 mL sealed tube in the microwave cavity at 150 °C (method B) until the reduction was completed, as determined by GC-MS or TLC. The reaction was cooled to rt and the crude mixture was treated with 0.5 M NaOH (25 mL) and extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, and the solvents were evaporated under reduced pressure. The corresponding aromatic amine **4** was obtained in pure form without further purification, unless otherwise stated, in the yields reported in Table 3. Characterization data and NMR spectra are presented in the Supporting Information.

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COMMUNICATION

Pinacol as a New Green Reducing Agent: Molybdenum-Catalyzed Chemoselective Reduction of Sulfoxides and Nitroaromatics

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

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