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Molybdenum-Catalyzed Deoxygenation of Heteroaromatic *N*-Oxides and Hydroxides using Pinacol as Reducing Agent

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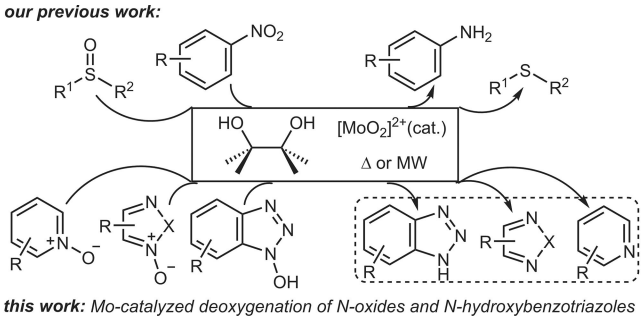
Abstract: A molybdenum-catalyzed deoxygenation of pyridine *N*-oxides and *N*-hydroxybenzotriazoles, as well as other azole *N*-oxides, has been developed using pinacol as an environmentally friendly oxo-acceptor. The only by-products are acetone and water making the process a convenient alternative to established protocols in terms of waste generation. The reaction is highly chemoselective and a variety of functional groups are tolerated. The processes are usually very clean allowing the isolation of the pure deoxygenated products after a simple extraction in most cases.

Keywords: amine *N*-oxides; deoxygenation; molybdenum; microwave heating; *N*-hydroxybenzotriazoles

The chemoselective deoxygenation of organic compounds such as sulfoxides and heteroaromatic *N*-oxides is of high importance in organic synthesis due to their great potential as intermediates in asymmetric synthesis and in the preparation of functionalized nitrogenated heterocycles, respectively.[1] Remarkably, the chemistry of heteroaromatic *N*-oxides has experienced a significantly increasing interest in recent years.[2] The negatively charged oxygen atom and the weakness of the N–O bond allow their efficient use as oxidants of alkynes in reactions catalyzed by gold, and other transition metal complexes.[3] In addition, they can behave as Lewis basic directing groups allowing valuable alternative C–H bond activations and as a consequence, the functionalization of *N*-oxides is becoming more useful in the synthesis of heterocycles.[4] Therefore, the development of efficient and eco-friendly methodologies for their deoxygenation remains an important goal considering that the major limiatations of the reported procedures for the reduction of heteroaromatic *N*-oxides are the use of toxic and/or expensive catalysts or reducing agents as well as harsh reaction conditions that many times are unsuitable for functionalized substrates.[5] In addition, the established methods commonly use trivalent phosphorous and boron reagents, or excess of reducing metals as oxygen acceptors, leading to considerable amounts of waste.

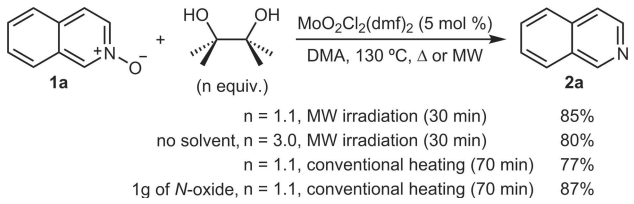
In this field we had previously reported that dioxomolybdenum(VI) complexes,[6] which are non-toxic and inexpensive compounds,[7] are useful catalysts for the chemoselective reduction of sulfoxides[8] and *N*-oxides,[5c] as well as for the reductive cyclization of nitroaromatics,[9] using phosphorous(III) reagents as oxygen-acceptors.[10] Looking for greener reducing agents in this area, we have more recently found that diols, including glycerol,[11] are also useful reagents for the deoxygenation of some of these compounds. We have mainly developed an efficient procedure for the chemoselective reduction of sulfoxides and nitroaromatics to the corresponding sulfides and anilines using pinacol (2,3-dimethyl-2,3-butanediol) as the oxo-acceptor and easily available dioxomolydenum(VI) complexes as catalysts.[12] Herein, we have updated this methodology to the deoxygenation of related and interesting *N*-oxides and *N*-hydroxybenzotriazoles (Scheme 1).

Based in the conditions developed for the Mo-catalyzed reduction of sulfoxides and nitroarenes with pinacol under microwave irradiation, we first explored the viability of the corresponding deoxygenation of isoquinoline *N*-oxide **1a**. Once some experiments were done, we observed complete conversion to isoquinoline after 30 min at 130 °C when using 1.1 equivalents of pinacol, 5 mol% of $MoO_2Cl_2(dmf)_2$ or $MoO_2Cl_2(dma)_2$ as catalyst and DMA as solvent.[13] Under these optimized conditions, isolation of isoquinoline with both high yield (85%) and purity was achieved by simple extraction with EtOAc/NaOH (0.3 M). This work-up completely removes the catalyst, the DMA and remaining pinacol as well as the



Scheme 1. Previous and present work.

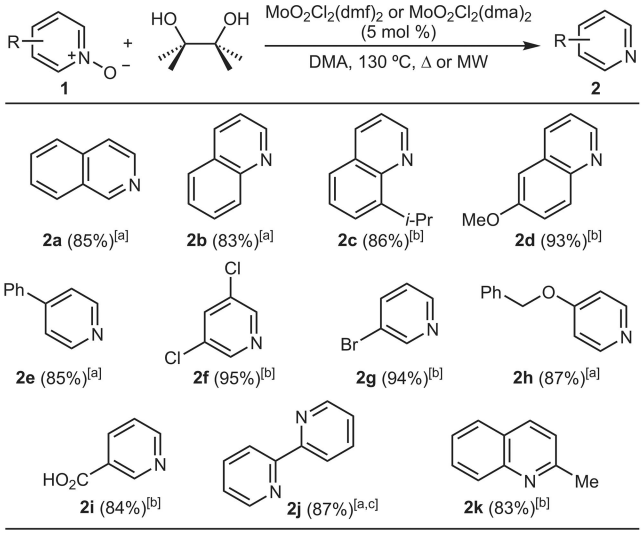
water and acetone generated as by-products. As expected, no appreciable reaction occurred in the absence of catalyst or pinacol whereas the use of 0.5 equiv. of the oxygen-acceptor reduces by half the reduction conversion. Reactions conducted at lower temperatures (90–110 °C) or catalyst loading (1.0 to 2.5 mol%) gave also low conversions (<40%) after 30 min. Interestingly, by increasing the amount of pinacol to 3 equivalents the reaction also proceeded to completion in the absence of additional solvent without affecting the reaction time or the isolated yield. Moreover, comparable results were obtained under conventional heating at the same temperature after 70 min even at gram scale (Scheme 2).



Scheme 2. [Mo]-catalyzed reduction of isoquinoline *N*-oxide **1a** with pinacol.

Using as optimal conditions 1.1 equivalents of pinacol, $MoO_2Cl_2(dmf)_2$ or $MoO_2Cl_2(dma)_2$ (5 mol%) as catalyst in DMA at 130 °C under microwave irradiation, reduction of a representative selection of heterocyclic *N*-oxides **1** with pinacol was examined and the results are illustrated in Scheme 3. Reactions of different quinoline and pyridine *N*-oxides **1a–k** occurred efficiently to afford the corresponding reduced products **2** in good to excellent yields after a simple extraction step and regardless of the electronic nature of their substituents. Moreover, the introduction of bulky groups close to the *N*-oxide unit did not affect the outcome of the reaction as illustrated with reactions of 8-*iso*-propylquinoline *N*-oxide **1c**, 2,2'-dipyridyl *N*,*N*'-dioxide **1j**, and 2-methylquinoline *N*-oxide **1k**. Notably, substrates possessing additional reducible functionalities such as halogens or acid **1f,g,i** were also chemoselectively reduced to the corresponding *N*-heterocycles **2f,g,i** with excellent yields (Scheme 3). The functional group tolerance displayed by this catalytic system is similar to the one we have previously observed when using Ph_3P as oxygen acceptor with the same metal complex as catalyst.[5c]

To further check the chemoselectivity of the developed reduction process, we performed selected experiments using 6-methoxyquinoline *N*-oxide **1d** as substrate in the presence of diverse functionalized additives and pinacol in equimolecular quantities (Scheme 4). Total chemoselectivity was observed for the reduction of the model quinoline *N*-oxide in the presence of potentially reducible groups such as halogens, aldehydes, ketones, esters, nitriles, sulfones, or acetylenes, since not even traces of conversion of these functional groups were detected. Remarkably, although the dioxomolybdenum(VI)-catalyzed deoxygenation of epoxides has been recently reported,[14] a selective reduction of **1d** was also observed in the presence of *trans*-stilbene oxide. At this point, taking into account our previous work on the deoxygenation of sulfoxides and nitroarenes with pinacol, using the same molybdenum catalysts and similar reaction conditions,[12] we wondered about the relative reactivity of these three functionalities: sulfoxides, nitroaromatics and *N*-oxides. Thus, we performed a reaction using an equimolecular mixture of 6-methoxyquinoline *N*-oxide **1d**, *p*-bromonitrobenzene and pinacol, under the optimized catalytic conditions, and we found that it exclusively evolved to produce 6-methoxyquinoline **2d** whereas the nitroaromatic compound remained unaltered. It should be noted that while the Mo-catalyzed reduction of nitroaromatics with pinacol occurred at 160–170 °C in DMA, lower temperature is required for *N*-oxides and so, the observed selectivity is not surprising. Finally, when an equimolecular mixture of **1d**, *p*-tolyl sulfoxide and pinacol was irradiated at 130 °C in the presence of the molybdenum catalyst, a high selectivity for the *N*-oxide reduction was observed as only minor amounts

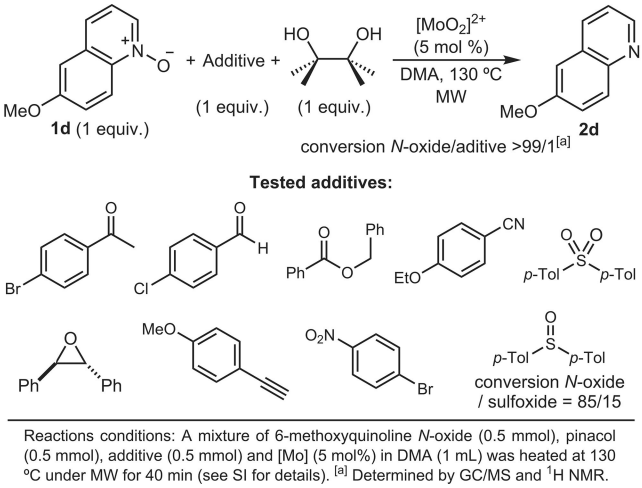


Reactions conditions: A mixture of *N*-oxide (0.5 mmol), pinacol (0.55 mmol) and [Mo] (5 mol%) in DMA (1 mL) was heated at 130 °C under MW for 30–40 min (see SI for details). [a] Reactions performed with $MoO_2Cl_2(dma)_2$. [b] Reactions performed with $MoO_2Cl_2(dmf)_2$. [c] Reaction conducted with 1.1 mmol (2.2 equiv.) of pinacol.

Scheme 3. [Mo]-catalyzed reduction of heterocyclic *N*-oxides with pinacol.

of *p*-tolyl sulphide were detected in the crude mixture. The observed selectivity can be explained on the basis of the higher basicity, and therefore a higher coordination ability to the Mo center, of *N*-oxides with respect to both sulfoxides and nitroaromatics.[15] These results reveal that *N*-oxides could be selectively deoxygenated under our developed reducing system, even in the presence of reducible functional groups.

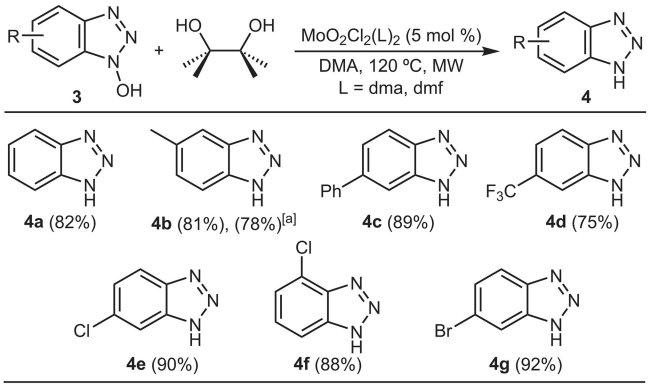
Although benzotriazoles are a very important type of heterocycles with a wide variety of applications in medicinal chemistry,[16] not many general methods for accessing *N*-unsubstituted benzotriazoles have been developed, including diazotation/cyclization of *o*-phenylenediamines,[17] and some other particular procedures that usually employ hazardous reagents and/or conditions.[18] Recently, Lakshman and Pottabathini



Reactions conditions: A mixture of 6-methoxyquinoline *N*-oxide (0.5 mmol), pinacol (0.5 mmol), additive (0.5 mmol) and [Mo] (5 mol%) in DMA (1 mL) was heated at 130 °C under MW for 40 min (see SI for details). [a] Determined by GC/MS and ^{1}H NMR.

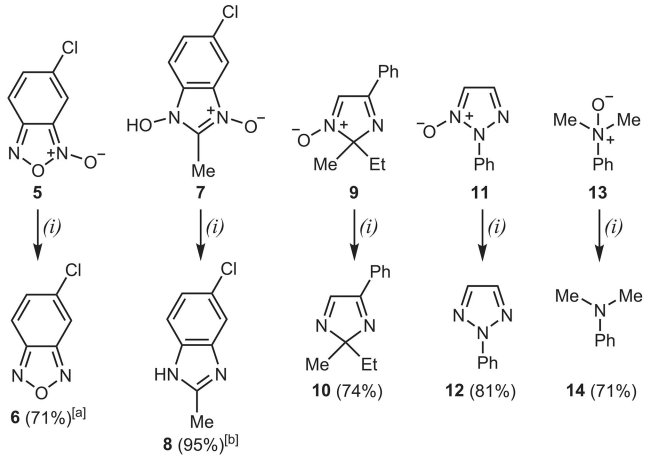
Scheme 4. [Mo]-catalyzed deoxygenation of 6-methoxyquinoline *N*-oxide **1d** with pinacol in the presence of additives sensitive towards reduction.

To check the applicability of our catalytic reducing protocol to other relevant *N*-heterocycles, we next turned our attention to *N*-hydroxybenzotriazoles. have reported a new sequence involving the deoxygenation of *N*-hydroxybenzotriazoles,[19] which are easily accessible from the reaction of *o*-halonitroaromatics



Reactions conditions: A mixture of *N*-hidroxybenzotriazole (0.5 mmol), pinacol (0.55 mmol) and [Mo] (5 mol%) in DMA (1 mL) was heated at 120 °C under MW irradiation for 15 min (see SI for details). [a] Reaction conducted for 30 min under conventional heating using 20 mol% of Mo catalyst.

Scheme 5. [Mo]-catalyzed reduction of *N*-hydroxybenzotriazoles **3** with pinacol.



(i) Reactions conditions: A mixture of the corresponding *N*-oxide (0.5 mmol), pinacol (0.55 mmol) and [Mo] (5 mol%) in DMA (1 mL) was heated at 120 or 130 °C under MW irradiation for the required time (see SI for details). [a] Isolated along with ~15% of a mixture of 4(5)-chloro-2-nitroaniline. [b] 2.2 equiv. of pinacol were used.

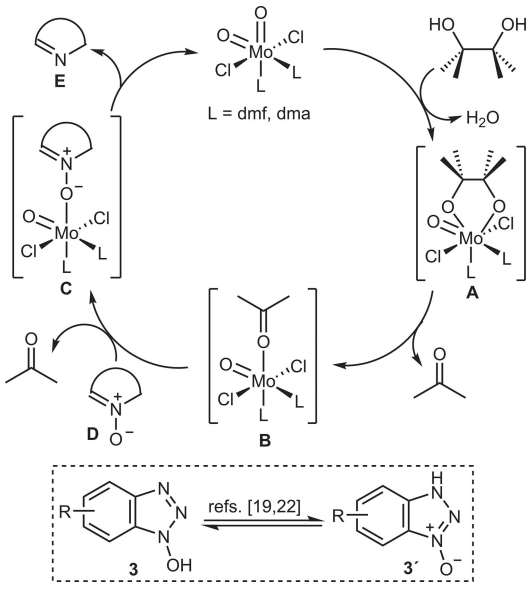
Scheme 6. [Mo]-catalyzed reduction of other *N*–O and *N*-hydroxy heterocycles with pinacol.

with hydrazine,[19,20] using tetrahydroxydiboron as reductant. Previously described methods involve the use of stoichiometric metals and/or harsh reaction conditions.[21] At this point, we wondered if our conditions for reducing $^{+}$N–O^{-} bonds could be applied to the N–OH→N–H reduction in *N*-hydroxybenzotriazoles taking into account that a prototropy could lead to a *N*-oxide tautomer, which is prone to behave in the same way. This prototropy had been previously proposed by Lakshman et al.,[19] and it is also known that the position of the *N*-oxide/*N*-hydroxy tautomeric equilibrium mainly depends on the polarity of the solvent, being shifted to the more polar *N*-oxide in polar solvents.[22] Pleasantly, under reaction conditions very similar to the ones developed for *N*-oxides, complete formation of benzotriazole **4a** was reached from *N*-hydroxybenzotriazole **3a** after 15 min in the MW cavity (Scheme 5). In this case, due to the high solubility of the benzotriazole in water the isolation of the reduced product was performed by column chromatography. Moreover, the combination of Mo(VI) catalyst/pinacol proved to be a general and selective reducing system for a range of *N*-hydroxybenzotriazoles **3** including halogen-functionalized substrates **3d–g** (Scheme 5). Thus, benzotriazoles **4** with substitution at different positions of the benzenoid moiety were obtained in good yields. In addition, reduction under conventional heating was also possible, although the catalyst loading had to be increased to 20 mol% to get the reaction to completion.

Finally, the reduction of other $^{+}$N–O^{-} and/or *N*-hydroxy heterocycles was explored using the developed procedure (Scheme 6). For instance, commercially available 5(6)-chlorobenzofuroxan **5** could be

deoxygenated to 5-chlorobenzo[*c*][1,2,5]oxadiazole **6** under the same reaction conditions, although minor amounts of 4(5)-chloro-2-nitroanilines were isolated along with **6.** In addition, 1-hydroxy-1*H*-benzimidazole 3-oxide derivative **7**, prepared by alkylation of benzofuroxan **5**,[23] could be doubly-reduced using excess of pinacol to benzimidazole **8** that was isolated in almost quantitative yield. However, selective mono-reduction to the corresponding 1-hidroxybenzimidazole with one equivalent of pinacol could not be achieved. In the same way, 2*H*-imidazole 1-oxides such as **9**,[24] as well as triazole *N*-oxides such as **11**,[25] were also efficiently deoxygenated to 2*H*-imidazole **10**[26] and 2*H*-1,2,3-triazole **12**, respectively. Finally, also *N*,*N*-dimethylaniline *N*-oxide **13**[27] could be deoxygenated to the corresponding aniline **14**, showing that this methodology is also suitable for non heteroaromatic *N*-oxides. These results further enhance the generality in the use of pinacol as convenient oxygen acceptor in combination with molybdenum catalysts.

The mechanism of these deoxygenation reactions may tentatively be proposed in analogy with our previous reported one for the deoxygenation of sulfoxides (Scheme 7).[12] This way, the catalyst $MoO_2Cl_2(L)_2$ first would react with pinacol likely giving rise to a pinacolate complex such as **A** and releasing a molecule of water. The pinacolate ligand could then be oxidatively cleaved by the Mo(VI) center leading to a new oxomolybdenum(IV) species **B**.[28] Immediate displacement of the weakly coordinated acetone by the corresponding *N*-oxide derivative **D**, which possesses an stronger coordination ability for the metal center, would afford a new complex **C**. The coordinated *N*-oxide would be able to reoxidize and regenerate the Mo(VI) catalyst, consequently releasing the deoxygenated heterocyclic compound **E** (Scheme 7). In the case of *N*-hydroxybenzotriazoles **3**, the tautomeric *N*-oxides **3'** could behave in the same way as the heteroaromatic *N*-oxides, giving rise after deoxygenation to 1*H*-benzotriazoles **4**. Moreover, the generation of acetone and water as by-products has been further confirmed by ^{1}H-NMR analysis of an experiment in which the deoxygenation of **1a** was carried out in dmf-d_7 (see Supporting Information).



Scheme 7. Proposed catalytic cycle for the [Mo]-catalyzed deoxygenation of *N*-heterocycles with pinacol.

In conclusion, we have demonstrated the value of pinacol as a green oxo-acceptor for the chemoselective deoxygenation of heteroaromatic *N*-oxides and *N*-hydroxybenzotriazoles under dioxomolybdenum(VI)-catalysis. Experimental advantages of the developed procedure include the use of a readily available and inexpensive catalyst, non-inert conditions, solvent-free protocol by using an excess of pinacol, and clean reactions that allow the isolation of most of the reduced compounds by a simple extraction. The results described herein significantly enhance the applicability of the environmentally friendly $[MoO_2]^{2+}$-catalyzed pinacol-mediated deoxygenation methodology, previously reported for sulfoxides and nitroaromatic compounds, by both increasing the reducible functional groups and the chemoselectivity, including the preferred deoxygenation of heteroaromatic *N*-oxides in the presence of sulfoxides or nitroarenes.

Experimental Section

General Procedure for Deoxygenation of *N*-Oxides 1 with Pinacol Catalyzed by $MoO_2Cl_2(dmf)_2$

A mixture of the corresponding *N*-oxide **1** (0.5 mmol), pinacol (65 mg, 0.55 mmol), and $MoO_2Cl_2(dmf)_2$ (8.6 mg, 0.025 mmol) in dry DMA (1 mL) was stirred at 130 °C for 60-70 min (method A), or irradiated in a 10 mL sealed tube in the microwave cavity at 130 °C for 30–40 min (method B). After completion of the reaction, determined by GC-MS or TLC, it was cooled to rt and the crude mixture was treated with 0.3 M aq. NaOH (10 mL) and extracted with EtOAc or Et_2O (3×15 mL). The combined organic layers were washed with 0.3 M aq. NaOH (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, and the solvents were removed under reduced pressure. The corresponding heterocycle **2** was obtained in pure form without further purification in the yields reported in Scheme 3. Characterization data and NMR spectra are presented in the Supporting Information.

Acknowledgements

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UPDATES

Molybdenum-Catalyzed Deoxygenation of Heteroaromatic *N*-Oxides and Hydroxides using Pinacol as Reducing Agent

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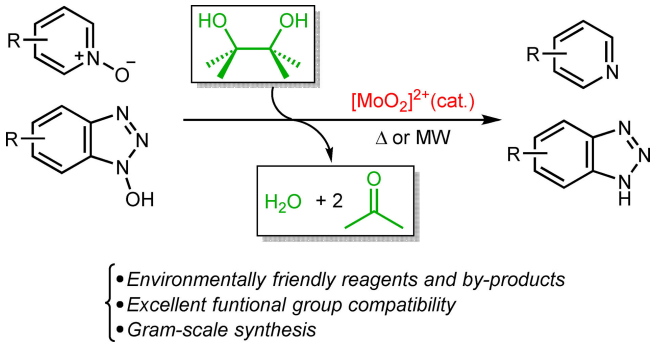

- *Environmentally friendly reagents and by-products*
- *Excellent funtional group compatibility*
- *Gram-scale synthesis*