SYNLETT
Spotlight 477

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

# Molybdenum(VI) Dichloride Dioxide

Compiled by Hari Krishna Kadam

Hari K. Kadam (born in Goa, India) obtained his M.Sc. (organic chemistry) with a gold medal in 2009 from Goa University and simultaneously cleared the CSIR-UGC NET JRF exam. Currently, he is working toward his Ph.D. in the field of synthetic organic chemistry under the supervision of Professor Santosh G. Tilve at Goa University. His research work is focussed on exploring new routes for the synthesis of nitrogen-containing bioactive organic compounds.

Department of Chemistry, Goa University, Taleigao Plateau, Goa 403206, India
E-mail: harikadam05@gmail.com

## Introduction

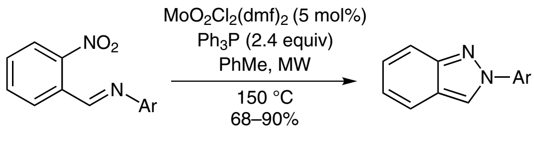
Although molybdenum(VI) dichloride dioxide ($MoO_2Cl_2$) has been known for a long time,[1] it is still exploited as a catalyst for versatile organic transformations.[2] It is an oxo-transfer catalyst, displaying its ability to promote oxidation as well as reduction reactions. In many reactions, it is also used as a Lewis acid.

## Preparation

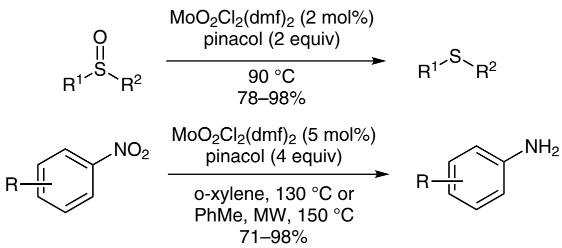
$MoO_2Cl_2$ is a pale-yellow solid, highly reactive and corrosive. It is commercially available[3] and can be prepared by a method reported by Colton and Tomkins.[4] $MoO_2Cl_2L_2$ (where L = dmf, dmso, and thf) are more frequently used because of their thermal and chemical stability. The preparation of $MoO_2Cl_2(dmf)_2$ is simple, efficient, and almost quantitative using readily available $Na_2MoO_4·2H_2O$.[5]

## Abstracts

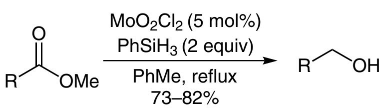
(A) Using catalytic $MoO_2Cl_2(dmf)_2$, arylindazoles are accessible by reductive cyclisation of *o*-nitrobenzylidene amines with triphenyl phosphine in refluxing toluene or under microwave conditions. Similarly, *o*-nitrostyrenes and nitrobiphenyls gave indoles and carbazoles, respectively. Benzothiazines, benzoxazines, and tetrahydroquinolines were obtained by the reductive cyclisation of ω-nitroalkenes via an Alder-ene reaction.[6]



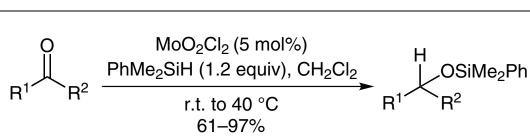

(B) Selective deoxygenation of sulfoxides to sulfides was carried out with triphenyl phosphate or boranes using $MoO_2Cl_2(dmf)_2$ or $MoO_2Cl_2$. Catalytic $MoO_2Cl_2(dmf)_2$ and pinacol as a benign reducing agent were used for the reduction of sulfoxides to sulfides. The same system was explored for the reduction of nitroaromatic compounds to anilines.[5,7]




(C) Aromatic and aliphatic esters were reduced to alcohols using silanes and catalytic $MoO_2Cl_2$. Imines were efficiently reduced to amines using the same system.[8]




(D) Using $MoO_2Cl_2$, dimethylphenylsilanes were added to aldehydes and ketones to give dimethylphenylsilylethers.[9]

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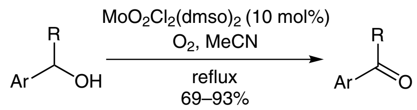
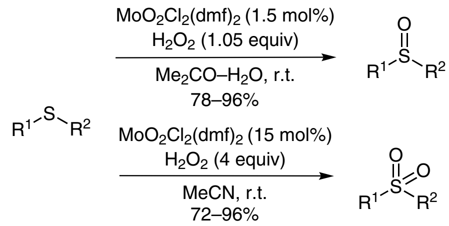
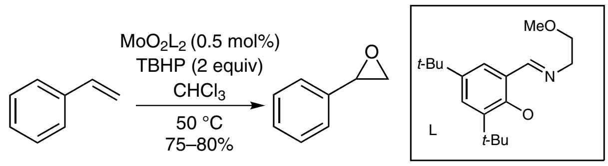
(E) $MoO_2Cl_2(dmso)_2$ is a mild oxidation catalyst and oxidizes primary benzylic alcohols to aldehydes and secondary alcohols to ketones using oxygen.[10]



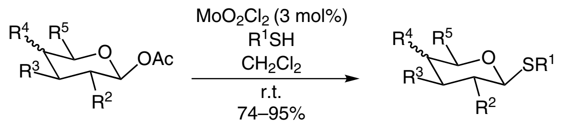

(F) Sulfides were selectively oxidized to sulfoxides and sulfones using $MoO_2Cl_2(dmf)_2$ as a catalyst and hydrogen peroxide in varying concentrations. Similarly, aliphatic and aromatic thiols were oxidized to disulfides.[11]



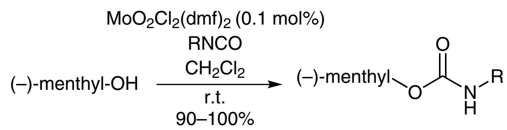

(G) Epoxidation of various internal and terminal alkenes was achieved with high selectivity and good yields using an oxo-Mo catalyst. Challenging substrates like styrenes were selectively and efficiently epoxidized.[12]



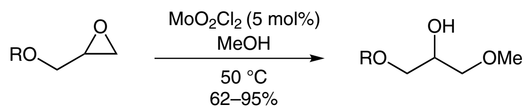

(H) Thioglycosylation of O-acetylated glycosides with functionalized thiols led to exclusive 1,2-*trans*-thioglycoside diastereomers using catalytic $MoO_2Cl_2$. β-Ketoesters were synthesized by $MoO_2Cl_2$-catalyzed condensation of ethyl diazoacetate and aldehydes. Acetylation, pivalation, and benzoylation of alcohols, amines, and thiols was achieved by nucleophilic acyl substitution using amphoteric $MoO_2Cl_2$ catalyst.[13]




(I) Carbamates were prepared from primary, secondary, or tertiary alcohols and aliphatic or aromatic isocyanates using low concentrations of $MoO_2Cl_2(dmf)_2$ catalyst. Optically active substrates were also explored with retention of configuration.[14]




(J) Methanolysis of epoxides to β-alkoxy alcohols is carried out by $MoO_2Cl_2$-catalyzed ring opening. Similarly, acetonidation or conversion of epoxides into α-alkoxyketones was also achieved.[15]




## References


(1) Berzelius, J. J. *Ann. Phys. Lpz.* **1826**, *46*, 381.
(2) Jeyakumar, K.; Chand, D. K. *J. Chem. Sci.* **2009**, *121*, 111.
(3) CAS No. 13637-68-8.
(4) Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1965**, *18*, 447.
(5) Sanz, R.; Escribano, J.; Aguado, R.; Pedrosa, M. R.; Arnáiz, F. J. *Synthesis* **2004**, 1629.
(6) (a) Moustafa, A. H.; Malakar, C. C.; Aljaar, N.; Merisor, E.; Conrad, J.; Beifuss, U. *Synlett* **2013**, *24*, 1573. (b) Sanz, R.; Escribano, J.; Pedrosa, M. R.; Aguado, R.; Arnáiz, F. J. *Adv. Synth. Catal.* **2007**, *349*, 713. (c) Malakar, C. C.; Merisor, E.; Conrad, J.; Beifuss, U. *Synlett* **2010**, 1766. (d) Huleatt, P. B.; Lau, J.; Chua, S.; Tan, Y. L.; Duong, H. A.; Chai, C. L. L. *Tetrahedron Lett.* **2011**, *52*, 1339.
(7) (a) Garcia, N.; Garcia, P. G.; Fernandez-Rodriguez, M. A.; Rubio, R.; Pedrosa, M. R.; Arnaiz, F. J.; Sanz, R. *Adv. Synth. Catal.* **2012**, *354*, 321. (b) Fernandes, A. C.; Romao, C. C. *Tetrahedron Lett.* **2007**, *48*, 9176.
(8) (a) Fernandes, A. C.; Romao, C. C. *J. Mol. Catal. A: Chem.* **2006**, *253*, 96. (b) Fernandes, A. C.; Romao, C. C. *Tetrahedron Lett.* **2005**, *46*, 8881.
(9) Fernandes, A. C.; Fernandes, R.; Romao, C. C.; Royo, B. *Chem. Commun.* **2005**, 213.
(10) Jeyakumar, K.; Chand, D. K. *Appl. Organometal. Chem.* **2006**, *20*, 840.
(11) (a) Sanz, R.; Aguado, R.; Pedrosa, M. R.; Arnáiz, F. J. *Synthesis* **2002**, 856. (b) Jeyakumar, K.; Chand, D. K. *Tetrahedron Lett.* **2006**, *47*, 4573.
(12) Judmaier, M. E.; Holzer, C.; Volpe, M.; Mosch-Zanetti, N. C. *Inorg. Chem.* **2012**, *51*, 9956.
(13) (a) Weng, S. S.; Lin, Y. D.; Chen, C. T. *Org. Lett.* **2006**, *8*, 5633. (b) Jeyakumar, K.; Chand, D. K. *Synthesis* **2008**, *11*, 1685. (c) Chen, C. T.; Kuo, J. H.; Pawar, V. D.; Munot, Y. S.; Weng, S. S.; Ku, C. H.; Liu, C. Y. *J. Org. Chem.* **2005**, *70*, 1188. (d) De Noronha, R. G.; Fernandes, A. C.; Romao, C. C. *Tetrahedron Lett.* **2009**, *50*, 1407. (e) Goswami, S.; Maity, A. C. *Tetrahedron Lett.* **2008**, *49*, 3092.
(14) (a) Stock, C.; Brückner, R. *Synlett* **2010**, 2429. (b) Stock, C.; Brückner, R. *Adv. Synth. Catal.* **2012**, *354*, 2309.
(15) Jeyakumar, K.; Chand, D. K. *Synthesis* **2008**, 807.