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

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Introduction

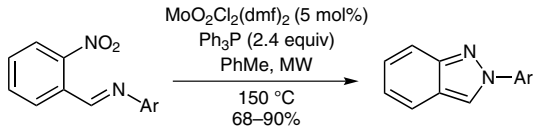
Although molybdenum(VI) dichloride dioxide (MoO_2Cl_2) has been known for a long time,[1] it is still exploited as a catalyst for versatile organic transformations.[2] It is an oxo-transfer catalyst, displaying its ability to promote oxidation as well as reduction reactions. In many reactions, it is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

Preparation

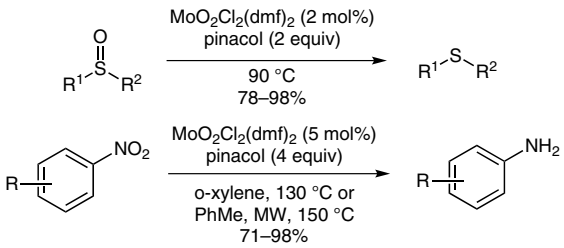
MoO_2Cl_2 is a pale-yellow solid, highly reactive and corrosive. It is commercially available[3] and can be prepared by a method reported by Colton and Tomkins.[4] $MoO_2Cl_2L_2$ (where L = dmf, dmso, and thf) are more frequently used because of their thermal and chemical stability. The preparation of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

Abstracts

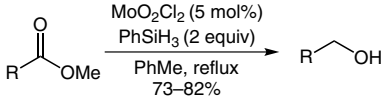
(A) Using catalytic $MoO_2Cl_2(dmf)_2$, arylindazoles are accessible by reductive cyclisation of *o*-nitrobenzylidene amines with triphenyl phosphine in refluxing toluene or under microwave conditions. Similarly, *o*-nitrostyrenes and nitrobiphenyls gave indoles and carbazoles, respectively. Benzothiazines,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



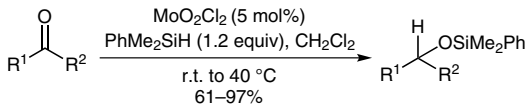
(B) Selective deoxygenation of sulfoxides to sulfides was carried out with triphenyl phosphate or boranes using $MoO_2Cl_2(dmf)_2$ or MoO_2Cl_2. Catalytic $MoO_2Cl_2(dmf)_2$ and pinacol as a benign reducing agent were used for the reduction of sulfoxides to sulfides. The same system was explored for 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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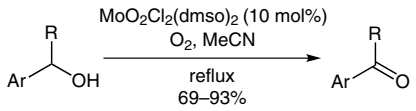
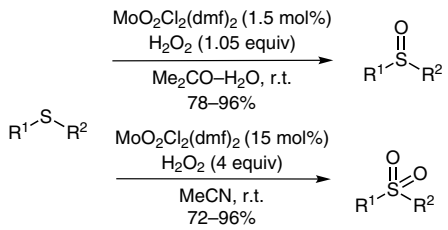
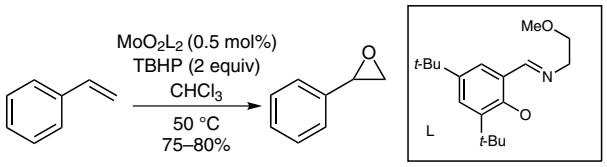
(E) $MoO_2Cl_2(dmso)_2$ is a mild oxidation catalyst and oxidizes primary benzylic alcohols to aldehydes and secondary alcohols to ketones using oxygen.[10]



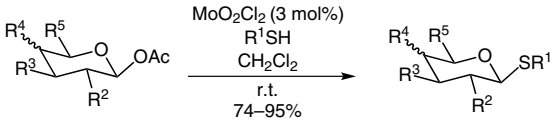
(F) Sulfides were selectively oxidized to sulfoxides and sulfones using $MoO_2Cl_2(dmf)_2$ as a catalyst and hydrogen peroxide in varying concentrations. Similarly, aliphatic and aromatic thiols were oxidized to disulfides.[11]



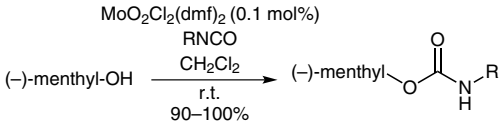
(G) Epoxidation of various internal and terminal alkenes was achieved with high selectivity and good yields using an oxo-Mo catalyst. Challenging substrates like styrenes were selectively and efficiently epoxidized.[12]



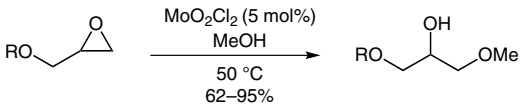
(H) Thioglycosylation of O-acetylated glycosides with functionalized thiols led to exclusive 1,2-*trans*-thioglycoside diastereomers using catalytic MoO_2Cl_2. β-Ketoesters were synthesized by MoO_2Cl_2-catalyzed condensation of ethyl diazoacetate and aldehydes. Acetylation, pivalation, and benzoylation 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]



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