SYNLETT Spotlight 477

Molybdenum(VI) Dichloride Dioxide

Compiled by Hari Krishna Kadam

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

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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 available³ and can be prepared by a method reported by Colton and Tomkins.⁴ $\text{MoO}_2\text{Cl}_2\text{L}_2$ (where L = dmf, dmsO, and thf) are more frequently used because of their thermal and chemical stability. The preparation of $\text{MoO}_2\text{Cl}_2(\text{dmf})_2$ is simple, efficient, and almost quantitative using readily available $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$.⁵

Abstracts

(A) Using catalytic $\text{MoO}_2\text{Cl}_2(\text{dmf})_2$, 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 $\text{MoO}_2\text{Cl}_2(\text{dmf})_2$ or MoO_2Cl_2 . Catalytic $\text{MoO}_2\text{Cl}_2(\text{dmf})_2$ 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 dimethylphenylsilyl ethers.⁹

(E) $\text{MoO}_2\text{Cl}_2(\text{dmsO})_2$ 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 $\text{MoO}_2\text{Cl}_2(\text{dmf})_2$ 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 $\text{MoO}_2\text{Cl}_2(\text{dmf})_2$ 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

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