SYNLETT Spotlight 477

Molybdenum(VI) Dichloride Dioxide

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Introduction

Although molybdenum(VI) dichloride dioxide (MoO$_2$Cl$_2$) 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$_2$Cl$_2$ 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$_2$Cl$_2$L$_2$ (where L = dmf, dmso, and thf) are more frequently used because of their thermal and chemical stability. The preparation of MoO$_2$Cl$_2$(dmf)$_2$ is simple, efficient, and almost quantitative using readily available Na$_2$MoO$_4·$2H$_2$O.$^5$

Abstracts

(A) Using catalytic MoO$_2$Cl$_2$(dmf)$_2$, arylindazoles are accessible by reductive cyclisation of α-nitrobenzylidene amines with triphenylphosphine in refluxing toluene or under microwave conditions. Similarly, α-nitrostyrenes and nitrobiphenyls gave indoles and carbazoles, respectively. Benzothiazines, benzoazoxines, and tetrahydroquinolines were obtained by the reductive cyclisation of α-nitroalkenes via an Alder-ene reaction.$^6$

(B) Selective deoxygenation of sulfoxides to sulfides was carried out with triphenylphosphate or boranes using MoO$_2$Cl$_2$(dmf)$_2$ or MoO$_2$Cl$_2$. Catalytic MoO$_2$Cl$_2$(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$_2$Cl$_2$. Imines were efficiently reduced to amines using the same system.$^8$

(D) Using MoO$_2$Cl$_2$, dimethylphenylsilanes were added to aldehydes and ketones to give dimethylphenylsilylethers.$^9$
(E) MoO$_2$Cl$_2$(dmsO)$_2$ is a mild oxidation catalyst and oxidizes primary benzyl alcohols to aldehydes and secondary alcohols to ketones using oxygen.$^{10}$

(F) Sulfides were selectively oxidized to sulfoxides and sulfones using MoO$_2$Cl$_4$(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$_2$Cl$_2$. β-Ketoesters were synthesized by MoO$_2$Cl$_2$-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$_2$Cl$_2$ catalyst.$^{13}$

(I) Carbamates were prepared from primary, secondary, or tertiary alcohols and aliphatic or aromatic isocyanates using low concentrations of MoO$_2$Cl$_2$(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$_2$Cl$_2$-catalyzed ring opening. Similarly, acetonidation or conversion of epoxides into α-alkoxyketones was also achieved.$^{15}$

References

(3) CAS No. 13637-68-8.