SYNLETT Spotlight 477

Molybdenum(VI) Dichloride Dioxide
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Introduction

Although molybdenum(VI) dichloride dioxide (MoO2Cl2) 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

MoO2Cl2 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 MoO2Cl2L2 (where L = dmf, dmso, and thf) are more frequently used because of their thermal and chemical stability. The preparation of MoO2Cl2(dmf)2 is simple, efficient, and almost quantitative using readily available Na2MoO4·2H2O.5

Abstracts

(A) Using catalytic MoO2Cl2(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, benzoazines, and tetrahydroquinolines were obtained by the reductive cyclisation of o-nitroalkenes via an Alder-ene reaction.6

(B) Selective deoxygenation of sulfoxides to sulfides was carried out with triphenyl phosphate or boranes using MoO2Cl2(dmf)2 or MoO2Cl2. Catalytic MoO2Cl2(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.7,8

(C) Aromatic and aliphatic esters were reduced to alcohols using silanes and catalytic MoO2Cl2. Imines were efficiently reduced to amines using the same system.9

(D) Using MoO2Cl2, dimethylphenylsilanes were added to aldehydes and ketones to give dimethylphenylsilyl ethers.9
(E) MoO$_2$Cl$_2$(dmoso)$_2$ 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$_2$Cl$_2$(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$_2$Cl$_2$-catalyzed condensation of ethyl diazocacetate 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) Methanalysis of epoxides to $\beta$-alkoxy alcohols is carried out by MoO$_2$Cl$_2$-catalyzed ring opening. Similarly, acetonidation or conversion of epoxides into $\alpha$-alkoxyketones was also achieved.$^{15}$

References

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