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Application of molybdenum(VI) dichloride dioxide (MoO_2Cl_2) in organic transformations

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Abstract. The role of MoO_2Cl_2 and some complexes containing MoO_2Cl_2 as catalysts for various Lewis acid catalysed organic transformations, oxidation and reduction reactions is reviewed.

Keywords. MoO_2Cl_2; catalysis; organic transformations.

1. Introduction

Molybdenum is a *d*-block transition metal sandwiched between chromium and tungsten in Group 6 and Period 5 of the Periodic Table which was isolated by Hjelm.[1] Molybdenite (MoS_2) is the most important ore of this element; others being wulfenite ($PbMoO_4$) and powellite ($CaMoO_4$).[2] The chemistry of molybdenum, whose compounds possess oxidation states of molybdenum ranging from (-II) to (VI) and coordination numbers from 4 to 8 leading to a diverse stereochemistry, is very versatile.[2,3] The variety of oxidation states and coordination numbers of molybdenum compounds can be enumerated by the representative examples: $[Mo(CO)_5]^{2-}$, $[Mo_2(CO)_{10}]^{2-}$, $Mo(CO)_6$, $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$, $[Mo(CNR)_7]^{2+}$, $[(RO)_3MoMo(OR)_3]$, $[Mo(CN)_8]^{4-}$, $MoCl_5$ and $MoOCl_4$. Molybdenum has the ability to form mono to polynuclear compounds with a variety of inorganic and organic ligands. The bi- and polynuclear compounds may contain Mo–Mo bonds and bridging ligands. It is this versatility which makes the chemistry of molybdenum challenging and exciting.

The potential applications of Mo-compounds are many.[3,4] Although molybdenum is sometimes described as a 'heavy metal', its properties are very different from those of the typical heavy metals (e.g. mercury, thallium and lead). Molybdenum is much less toxic than these and already found application as an alternative substitute for some heavy metals. Molybdenum has also found application in materials like pigments,[5,6] corrosion inhibitors,[3] smoke suppressants,[7] lubricants[3] and fertilizers.[8]

In addition to this, molybdenum-based catalysts have a number of important applications in the petroleum and plastic industries. A major use is in the hydrodesulfurisation (HDS) of petroleum, petrochemicals and coal-derived liquids. Molybdenum catalysts are resistant to poisoning by sulfur and hence used for conversion of hydrogen and carbon monoxide to alcohols even in the presence of sulfur which would poison precious metal catalysts. Similarly, molybdenum based catalysts have been used in the conversion of coal to hydrocarbon liquids. Several catalysts based on molybdenum have been exploited in a number of organic transformations which are recently reviewed by Prabhu *et al.*[9a] and Khurana *et al*.[9b]

Recently, molybdenum(VI) dichloride dioxide (MoO_2Cl_2) has been used as an efficient catalyst for several organic transformations. In this review, we describe the synthesis and applications of MoO_2Cl_2 and related adducts/complexes as catalysts for various Lewis acid catalysed organic transformations, oxidation and reduction reactions.

2. Molybdenum(VI) dichloride dioxide

The known chlorides of molybdenum are $MoCl_2$, $MoCl_3$, $MoCl_4$, $MoCl_5$ and $MoCl_6$ where as the available oxochlorides are $MoOCl_4$, MoO_2Cl_2, $MoOCl_3$ and MoO_2Cl. These oxochlorides are prepared by a range of oxygenation and chlorination reactions. Among the various oxohalides of molybdenum, molybdenum(VI) dichloride dioxide (MoO_2Cl_2) received much attention in chemistry.

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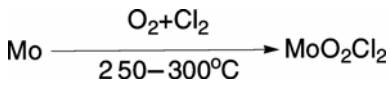
MoO_2Cl_2 was synthesized by Berzelius in 1826.[10] Alternative and better methods for the synthesis of MoO_2Cl_2 was reported by Colton and Tomkins in 1965.[11] According to Colton and Tomkins, a 1 : 1 mixture of dry oxygen and chlorine was passed over Mo at 250–350°C (scheme 1) and the resulting white volatile product was purified by sublimation to obtain MoO_2Cl_2. This compound is a pale yellow solid which is available commercially from few suppliers including Aldrich.

The molecular structure of gaseous MoO_2Cl_2 is distorted tetrahedral as determined by electron diffraction studies (figure 1).[12,13] The solid state structure contains –(O : Mo–O : Mo)– chains in two directions and the structure is laminar with a network of alternating O and Mo atoms[14] with hexa-coordinated metal centers. Thus, MoO_2Cl_2 can form complexes with suitable ligands to provide hexa-coordinated geometries.[15] Hepta-coordinated structures are also claimed e.g. with benzyl amine as ligand.[16]

2.1 *Complexation of molybdenum(VI) dichloride dioxide with various ligands*

Typical ligands and coordinating solvents, can fill the available positions around the metal centre of MoO_2Cl_2 to form complexes of general formulae $MoO_2Cl_2(\mathbf{L})_2$ and $MoO_2Cl_2(\mathbf{L})$ for mono and bidentate ligands, respectively. The complexes are distorted octahedral with the oxo ligands positioned *cis* to each other. Usually, the anionic chlorides are *trans* to each other whereas the remaining two sites are coordinated by ligand(s) in a *cis* manner. This gives the *cis*-oxo, *trans*-Cl, *cis*-**L** geometry (figure 2).[17]

However, there are exceptions and compounds with all *cis* configurations have also been isolated.[17] Compounds of other possible formula obtained from the complexation of MoO_2Cl_2 with a variety of ligands are known, as dictated by the nature of the ligand. Tridentate ligand such as *tris*(pyrazolyl)borate on complexation with MoO_2Cl_2 replaces one of the chlorides leading to the formation of octahedral $[MoO_2Cl(\mathbf{L})]$.[18] Two units of a bidentate ligand may replace both the chloride ions as observed with *o*-phenylene diamine to give octahedral $MoO_2(\mathbf{L})_2$.[19] Interestingly, a four coordinated compound $MoO_2(OAr)_2$ was obtained by using a hindered aryloxide ligand where both the chlorides are replaced.[20] In fact, removal of both the chlorides and one oxo from MoO_2Cl_2 is reported with a less hindered aryloxide ligand where a penta-coordinated compound $MoO(OAr)_4$ is resulted.[21]



Scheme 1. Synthesis of molybdenum(VI) dichloride dioxide.

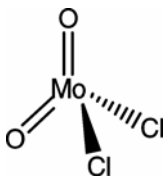


Figure 1. Structure of MoO_2Cl_2.

2.2 *Applications of MoO_2Cl_2 in various organic transformations*

Although MoO_2Cl_2 is known for a long time, this compound is being exploited as catalyst for organic transformations in recent years. To the best of our knowledge, the early studies on the catalytic behavior of MoO_2Cl_2 are documented as three patents[22–24] where the catalyst was employed in presence of external reagents for epoxidation of olefins. Subsequently, some more reports on epoxidation reactions using MoO_2Cl_2,[25,26] and β-ketophosphonate com-

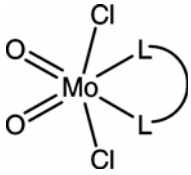
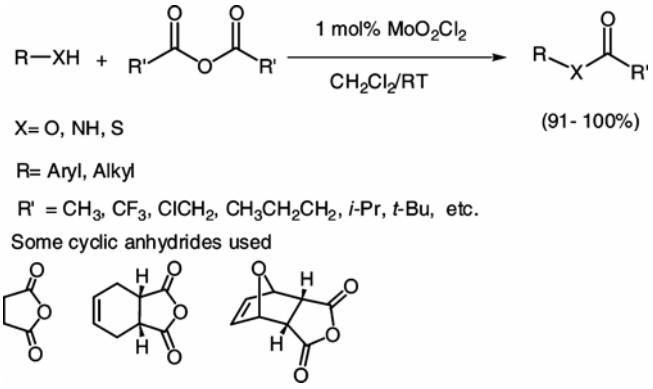


Figure 2. Structure of *cis-trans-cis*-$MoO_2Cl_2(\mathbf{L})_2$.



Scheme 2. Acylation of alcohols, amines and thiols using MoO_2Cl_2.

plexes[27] appeared. Oxidation of PPh_3 was achieved by the oxo-transfer behaviour of $MoO_2Cl_2(dmso)_2$.[28] Essentially, these reports show the ability of MoO_2Cl_2 and related compounds as oxo-transfer catalysts. However, the scope of the reactions and other possible organic transformations were not studied until the beginning of the current decade. This section, reviews the recent developments on the use of MoO_2Cl_2 and its complexes as catalysts for organic transformations.

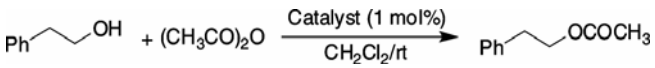
2.2a *Acylation reactions*: MoO_2Cl_2 acts as an efficient amphoteric catalyst to facilitate nucleophilic acyl substitution of anhydrides with a variety of alcohols, amines and thiols in high yields and high chemoselectivity (scheme 2).[29] Acylations went smoothly with primary, secondary, and acid-sensitive allylic and benzylic alcohols. Tertiary alcohols such as *tert*-butyl alcohol and trityl alcohol were completely inert towards acylation with catalytic MoO_2Cl_2 at ambient temperature. However, *tert*-butylamine and *tert*-butanethiol were fairly reactive under these reaction conditions. Aromatic alcohols, amines, and thiols were amenable to acylations in essentially quantitative yields.

Acetylation of 2-phenylethanol was carried out by using acetic anhydride in presence of various commercially available Group 6 oxometallic species such as $MoOCl_4$, $WOCl_4$, CrO_2Cl_2, $MoO_2(acac)_2$ and WO_2Cl_2 as catalyst.[29] It was observed that MoO_2Cl_2 is the most reactive catalyst among the oxometallic species used for the acetylation reaction (table 1).[29]

The proposed mechanism for MoO_2Cl_2 catalysed acylation reaction is shown in scheme 3. The first step of the esterification reaction is nucleophilic attack of the lone pair on the oxygen of MoO_2Cl_2 to the carbonyl carbon of the acid anhydride. The second step is also a nucleophilic attack where the alcohol reacts with the metalate-carboxylic acid mixed anhydride (figure 3) to release the products.

2.2b *Thioglycosylation of functionalized peracetylated glycosides:* MoO_2Cl_2 was found as an efficient catalyst for the thioglycosylation of *O*-acetylated glycosides with functionalized thiols in dichloromethane at room temperature (scheme 3).[30] The obtained products were found to be 1,2-*trans*-thioglycosides with exclusive diastereocontrol.

Table 1. Acetylation of 2-phenylethanol catalysed by some Group 6 oxometallic species.



Entry	Catalyst	Time (h)	t_{12}[a]	Yield (%)[b]
1	$MoOCl_4$	0·08	40 s	97
2	$WOCl_4$	28	6·8 h	96
3	CrO_2Cl_2	7	2.1 h	100
4	MoO_2Cl_2	0·05	7 s	100
5	$MoO_2(acac)_2$	10	2·5 h	98
6	WO_2Cl_2	47	16·8 h	100

[a]The reaction time at 50% conversion. [b]Isolated yields

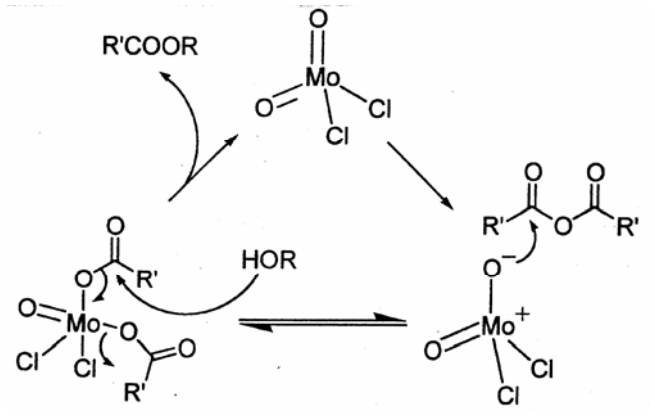
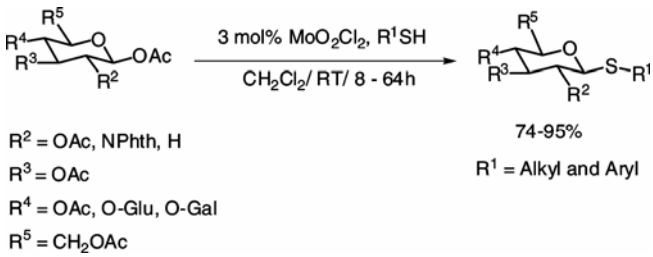
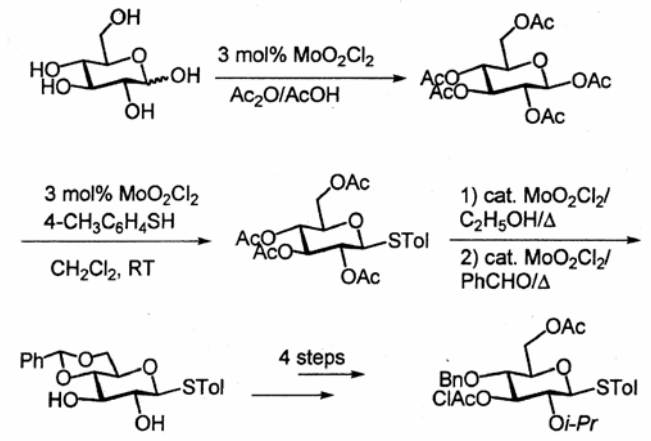


Figure 3. Proposed mechanism for acylation reactions catalysed by MoO_2Cl_2.



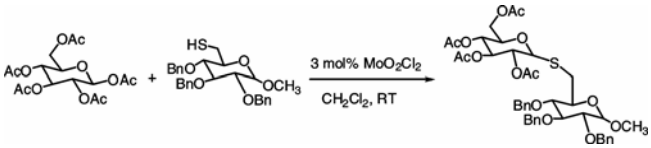
Scheme 3. Thioglycosylation of *O*-acetylated glycolsides with thiols using MoO_2Cl_2.



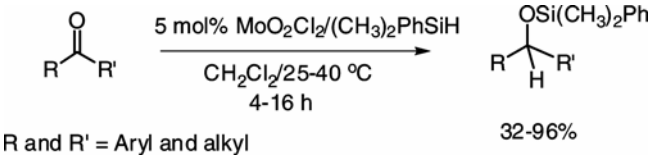
Scheme 4. Synthesis of a universal glycoside building block.

The new catalytic protocol was applied for the synthesis of a mono-glycoside building block (scheme 4)[30] and β-(1→6)-*S*-linked-thiodisaccharide (scheme 5).[30]

2.2c *Hydrosilylation of aldehydes and ketones:* MoO_2Cl_2 catalyses the addition of dimethylphenylsilane $(CH_3)_2PhSiH$ to aldehydes and ketones to afford the corresponding dimethylphenylsilyl ethers in good yields (scheme 6).[31,32] Though several dioxomolybdenum(VI) compounds act as catalysts (e.g. $MoO_2(acac)_2$, $MoO_2(S_2CNEt_2)_2$, etc.) for hydrosilylation of aromatic and aliphatic aldehydes and ketones, MoO_2Cl_2 was found to be most active.[32]



Scheme 5. A representative synthesis of β-(1→6)-*S*-linked-thiodisaccharide.



Scheme 6. Hydrosilylation of aldehydes and ketones using MoO_2Cl_2.

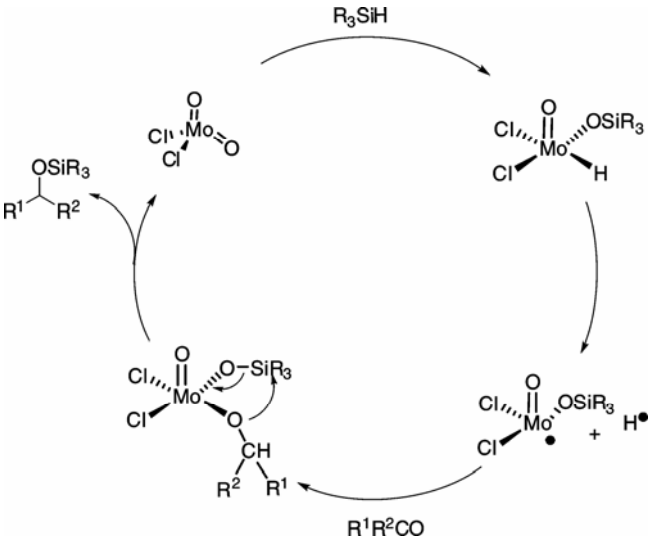
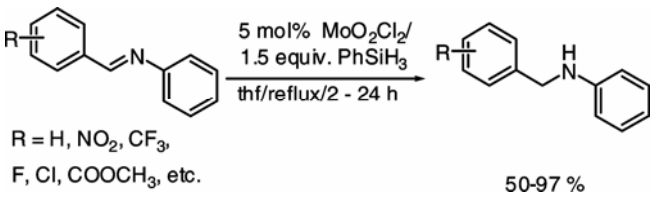


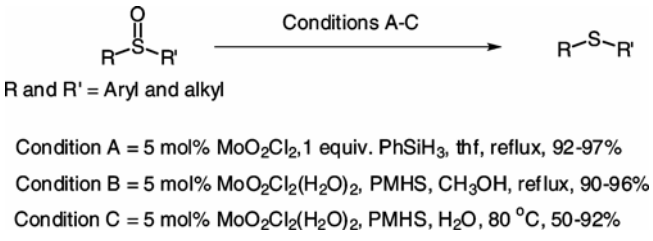
Figure 4. Proposed mechanism for MoO_2Cl_2 catalysed hydrosylilation reactions.

The proposed mechanism for the MoO_2Cl_2 catalysed hydrosilylation of aldehydes is shown in figure 4.[32] The first step can be described as activation of Si–H bond by MoO_2Cl_2 to form the hydride species, $[MoCl_2H(O)(OSiR_3)]$ via [2 + 2] addition. Further, the hydride species undergoes homolytic cleavage of Mo–H bond to produce the metal and hydrogen radicals which undergoes addition with aldehyde followed by elimination to give the hydrosilylated product (figure 4).[32]

2.2d *Reduction of imines:* MoO_2Cl_2 was used as an efficient catalyst for the reduction of imines in the presence of various silanes including phenylsilane, dimethylphenylsilane, triethylsilane, triphenylsilane and polymethylhydrosiloxane in different solvents.[33] The best result was obtained with phenylsilane in the presence of 10 mol% of MoO_2Cl_2 in thf under reflux condition (scheme 7). Under this optimized reaction condition, various imines were chemoselectively reduced to give the corresponding amines in the presence of nitro, halo and ester functionalities.



Scheme 7. Reduction of various imines using silane/MoO_2Cl_2.



Scheme 8. Reduction of sulfoxides using silane/MoO_2Cl_2.

Scheme 9. Reduction of sulfoxides using borane/MoO_2Cl_2.

2.2e *Reduction of sulfoxides:* Sulfoxides were reduced to corresponding sulfides using MoO_2Cl_2/silane system under three different reaction conditions (scheme 8).[34] Various aryl-aryl, aryl-alkyl, alkyl-alkyl sulfoxides were reduced to corresponding sulfides in high yields. During the reduction of sulfoxides halo, carboxyl and vinyl functional groups were found to be stable.[34]

In addition to this report, catecholborane/$MoO_2Cl_2(H_2O)_2$ and BH_3·thf/MoO_2Cl_2 systems were also used for the reduction of sulfoxides to the corresponding sulfides (scheme 9).[35]

Author has proposed the mechanism for reduction of sulfoxides using MoO_2Cl_2/borane systems (figure 5).[35] The first step is considered as activation of B–H bond by MoO_2Cl_2, which is similar to first step of hydrosylilation reactions (see figure 4). In the second step, generation of molybdenum(IV) species from the molybdenum–borane complex is proposed which also co-ordinates with the sulfoxides. The sulfide is released where upon the catalyst is regenerated in the last step (figure 5).

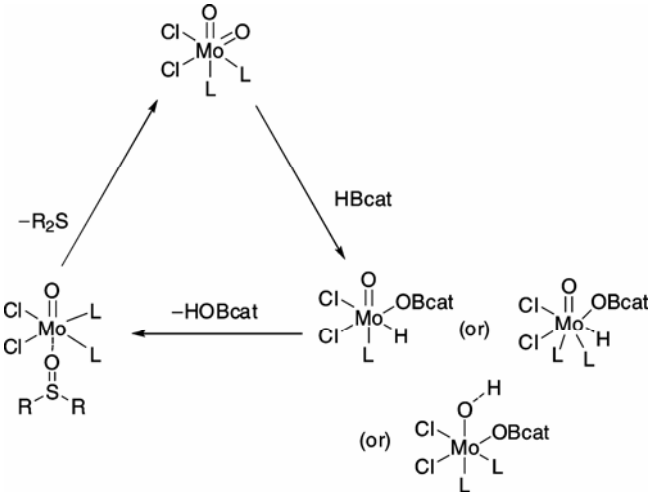
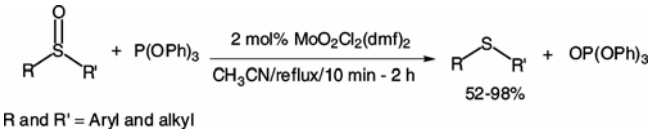
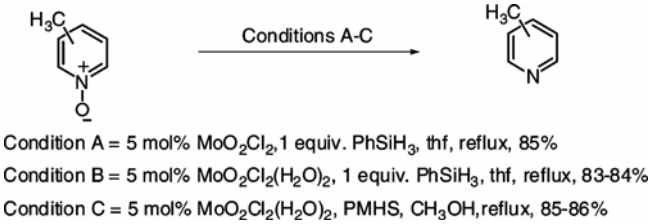


Figure 5. Proposed mechanism for the reduction of sulfoxides using MoO_2Cl_2/borane.



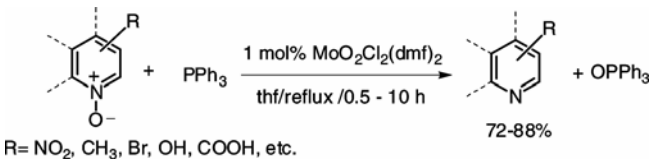
Scheme 10. Deoxygenation of sulfoxides to sulfides.



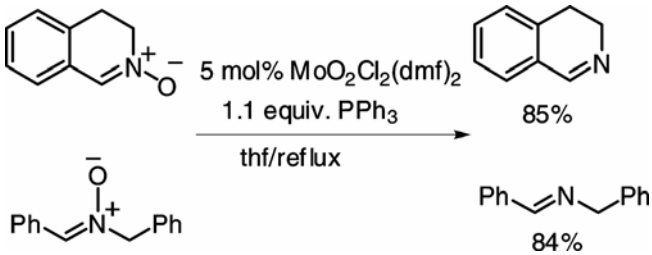
Scheme 11. Reduction of pyridine *N*-oxides using silane/MoO_2Cl_2.

Reduction of sulfoxides to sulfides is also reported with $MoO_2Cl_2(dmf)_2$ in the presence of $P(OPh)_3$ (scheme 10).[36] The reactions were carried out under reflux conditions in CH_3CN using 2 mol% of $MoO_2Cl_2(dmf)_2$ with 1·1 equiv. of $P(OPh)_3$. Dialkyl sulfoxides were deoxygenated in a few minutes whereas diaryl sulfoxides needed between 30 min and 2 h depending on the electronic and steric characteristics of the sulfoxides. In particular, the reduction of dibenzyl sulfoxide serves as a measure of the utility of the reaction, since many methods either fail completely with this substrate or provide only poor yields of dibenzyl sulfide.

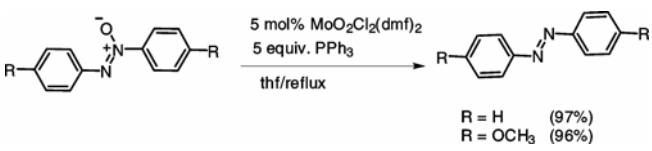
The sulfoxides possessing β-keto and β-ethoxy carbonyl functionalities were chemoselectively reduced to the corresponding sulfides in good yields without affecting the carbonyl functionalities.[36] Moreover, hydroxy, allyl and propargyl functionalities also remained intact under the reduction conditions.[36]



Scheme 12. Deoxygenation of *N*-oxides.



Scheme 13. Deoxygenation of nitrones.



Scheme 14. Deoxygenation of azoxybenzenes.

2.2f *Reduction of N-oxides:* MoO_2Cl_2 was also utilized as a catalyst for reduction of pyridine-*N*-oxides with silane under three different reaction conditions (scheme 11).[34] The reactions were carried out under reflux condition using 5 mol% of catalyst with 1 equiv. of phenylsilane ($PhSiH_3$) or 0.3 equiv. of polymethylhydrosiloxane (PMHS).[34]

Chemoselective deoxygenation of *N*-oxides was carried out under mild conditions with triphenyl phosphines in the presence of $MoO_2Cl_2(dmf)_2$ (scheme 12).[37] Efficient deoxygenation of several aromatic *N*-oxides were achieved in 75–88% yields.

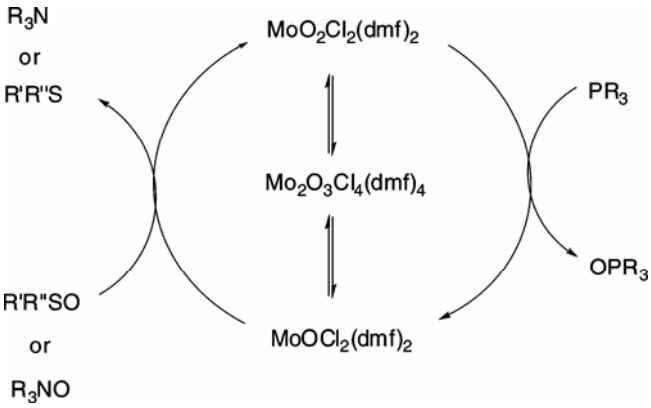
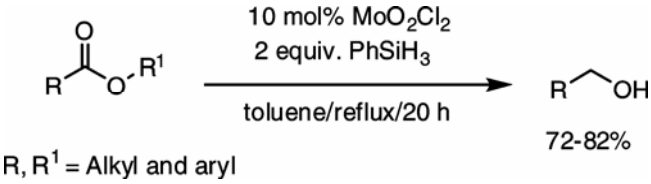
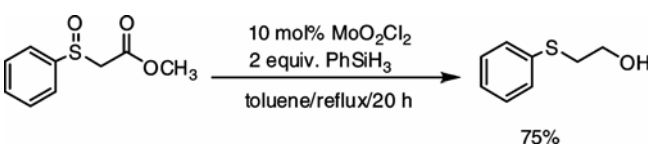


Figure 6. Proposed mechanism for deoxygenation of sulfoxides and *N*-oxides.



Scheme 15. Reduction of esters using silane/MoO_2Cl_2.

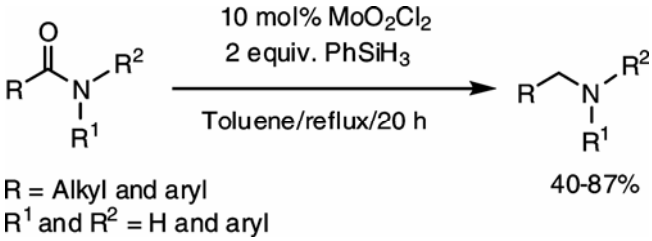
Scheme 16. Reduction of methyl 4-nitrobenzoate.



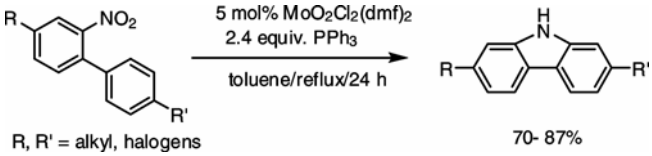
Scheme 17. Reduction of methyl-(phenylsulfinyl) acetate.

This methodology was extented to deoxygenation of nitrones (scheme 13) and azoxybenzenes (scheme 14).[37] During the deoxygenation of nitrones and azoxybenzenes, 5 mol% of the catalyst was used. Also, large excess of PPh_3 was used for the reduction of azoxy derivatives.[37]

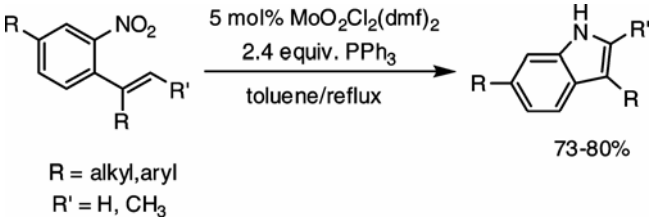
Sanz *et al* proposed the mechanism for deoxygenation of sulfoxides and *N*-oxides using $MoO_2Cl_2(dmf)_2/R_3P$ as shown in figure 6.[36,37] In the first step $MoO_2Cl_2(dmf)_2$ undergoes reduction to form $MoOCl_2(dmf)_2$ in the presence R_3P which could be in equilibrium with $Mo_2O_3Cl_4(dmf)_4$. In the second step, $MoOCl_2(dmf)_2$ takes one oxygen from the sulfoxides



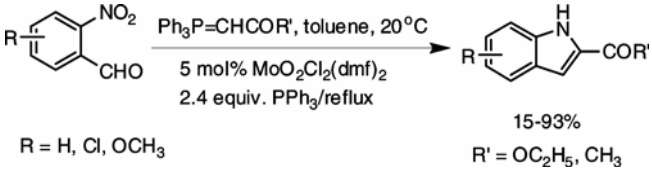
Scheme 18. Reduction of amides using silane/MoO_2Cl_2.



Scheme 19. Synthesis of carbazoles by reductive cyclization of nitroaromatics.



Scheme 20. Synthesis of indoles by reductive cyclization of nitroaromatics.



Scheme 21. One-pot synthesis of functionalized indoles.

or *N*-Oxides to effect the reduction of the substrate and sustain the catalytic cycle.[36,37]

2.2g *Reduction of esters:* The system, $PhSiH_3$/MoO_2Cl_2 was investigated for the reduction of a variety of esters in toluene under reflux conditions (scheme 15).[38] Aromatic and aliphatic esters were reduced to corresponding alcohols in good yields. One exception was observed in the reduction of methyl 4-nitrobenzoate, which afforded methyl 4-aminobenzoate in 50% yield (scheme 16). The reaction of methyl-(phenylsulfinyl)acetate with this system yielded the 2-(phenylthio)ethanol in 75% yield with reduction of both sulfinyl and carboxyl groups (scheme 17).

2.2h *Reduction of amides:* A novel method for the reduction of amides to the corresponding amines using a silane/MoO_2Cl_2 system is reported (scheme 18).[39] The reduction of a variety of primary, secondary and *tert*-amides was investigated with 10 mol% MoO_2Cl_2 in the presence of $PhSiH_3$ under reflux condition in toluene. This method was found to be suitable for the reduction of *tert*-amides with bulky *N*-substituents where as primary and secondary amides gave relatively low yields.[39]

2.2i *Reductive cyclization of nitroaromatics to carbazoles and indoles:* $MoO_2Cl_2(dmf)_2$ catalysed reductive cyclization of nitrobiphenyls and nitrostyrenes were carried out in the presence of triphenylphosphine to achieve carbazoles and indoles, respectively (schemes 19–21).[40] The reactions were carried out under reflux conditions in toluene, where wide range of interesting functionalized carbazole and indole derivatives have been prepared without affecting the various sensitive functional groups such as alkyls, ethers, carbonyls, halogens and carboxylic esters.

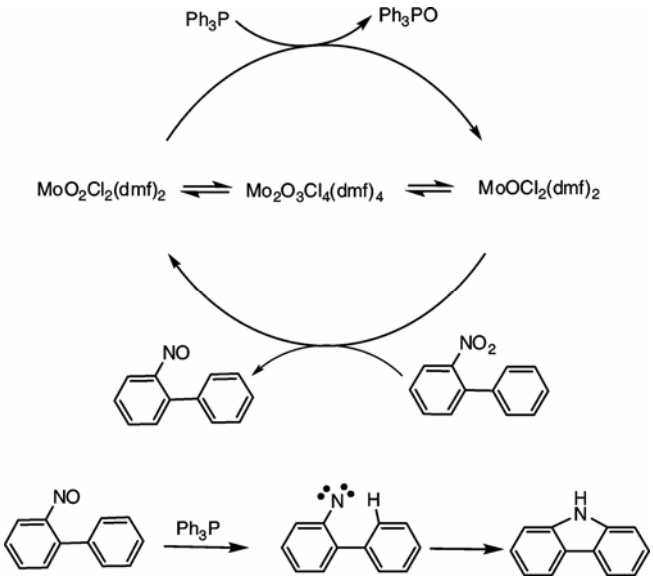
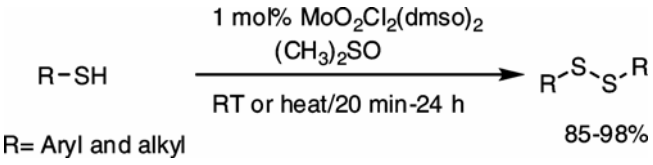


Figure 7. Proposed mechanism for reductive cyclization of nitroaromatics.



Scheme 22. Oxidation of thiols to disulfides.

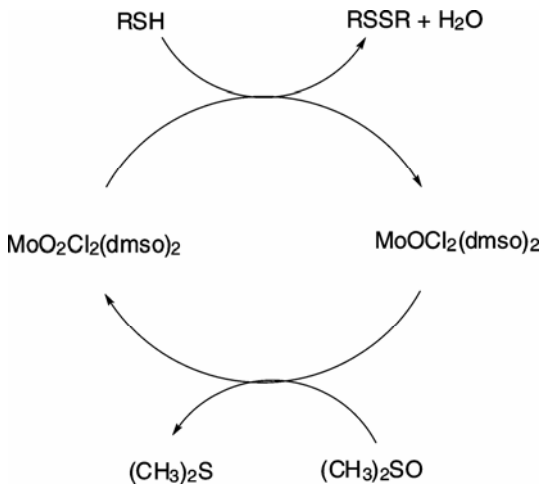
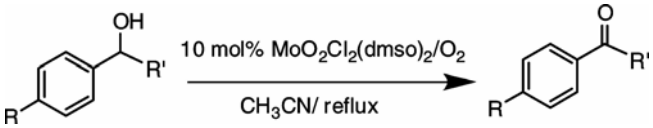


Figure 8. Proposed mechanism for oxidation of thiols by $MoO_2Cl_2(dmso)_2$.



Entry	R	R′	Time (h)	Yield (%)[a]
1	OCH_3	H	2·5	91
2	$N(CH_3)_2$	H	2·5	91
3	SCH_3	H	3	93
4	H	H	5	< 5
5	NO_2	H	5	< 5
6	H	CH_3	5	83
7	NO_2	CH_3	7	71

[a]Isolated yield

Scheme 23. Oxidation of benzylic alcohols with $MoO_2Cl_2(dmso)_2$.

One-pot synthesis of regioselectively functionalized indoles has also been developed from 2-nitrobenzaldehydes and Wittig reagents (scheme 21).

The mechanistic aspects of the transformation is proposed (figure 7) where the first step is the reduction of dioxomolybdenum(VI) by PPh_3. The resulting oxomolybdenum(IV) reacts with nitro group and provides nitroso intermediates. The nitroso intermediate then undergoes reductive cyclization to carbazoles which is facilitated by PPh_3.

2.2j *Oxidation of thiols to disulfides:* $MoO_2Cl_2(dmso)_2$ catalysed oxidation of thiols to disulfides in dmso at room temperature or elevated temperature is reported (scheme 22).[41] Various aromatic thiols were oxidized to corresponding disulfides at room temperature using 1 mol% of the catalyst. Non-aromatic thiols were oxidized to corresponding disulfides at 70°C using 5 mol% of the catalyst. The procedure, though involve the production of dimethyl sulfide, is attractive because of its simplicity, general applicability and excellent yields of the products, making it a useful addition to the existing methodologies.

The proposed mechanism for thiol oxidation is shown in figure 8. The thiol undergoes an oxidative coupling to form corresponding disulfide as assisted by the dioxomolybdenum(VI) complex which in turn is reduced to an oxomolybdenum(IV) species. Then DMSO reoxidizes Mo(IV) to Mo(VI) with the release of dimethyl sulfide.

2.2k *Oxidation of alcohols with MoO_2Cl_2(**L**)$_2$ (where L = dmso, dmf and thf):* $MoO_2Cl_2(\mathbf{L})_2$ (where L = dmso, dmf and thf) were used as selective catalyst for the oxidation of secondary and activated primary benzyl alcohols (scheme 23).[42] The reactions were carried out using 10 mol% of catalyst while bubbling of oxygen under reflux conditions in acetonitrile. Among these catalysts i.e. $MoO_2Cl_2(\mathbf{L})_2$ (where L = dmso, dmf and thf), dmso adduct is found to be more efficient. Secondary and activated primary benzyl alcohols were oxidized to corresponding aldehydes and ketones in good yields. This method is found to be selective for the oxidation of secondary and activated primary benzyl alcohols, where as unactivated and deactivated primary benzyl alcohols remained almost intact.

A proposed reaction mechanism is shown in figure 9.[42] The possible addition of OH group across the Mo–O double bond of the solvated catalyst is the first step. The Mo(VI) center then undergoes reduction to Mo(IV) by eliminating carbonyls along with H_2O. Further, the intermediate Mo(IV) species could be reoxidized by oxygen regenerating the catalyst. In this work, benzyl alcohol could not be oxidized even under oxygen bubbling condition. Thus, the presence of electron releasing group in the benzyl alcohol is responsible to initiate the addition for the subsequent steps of the catalysed reactions.

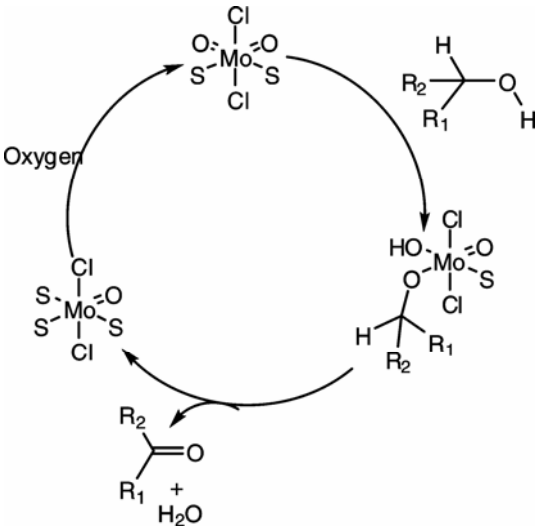
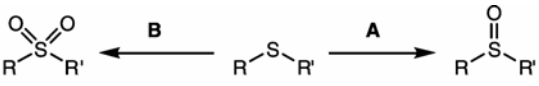


Figure 9. Proposed mechanism for $MoO_2Cl_2(dmso)_2$ catalysed alcohol oxidation. (S = solvent).



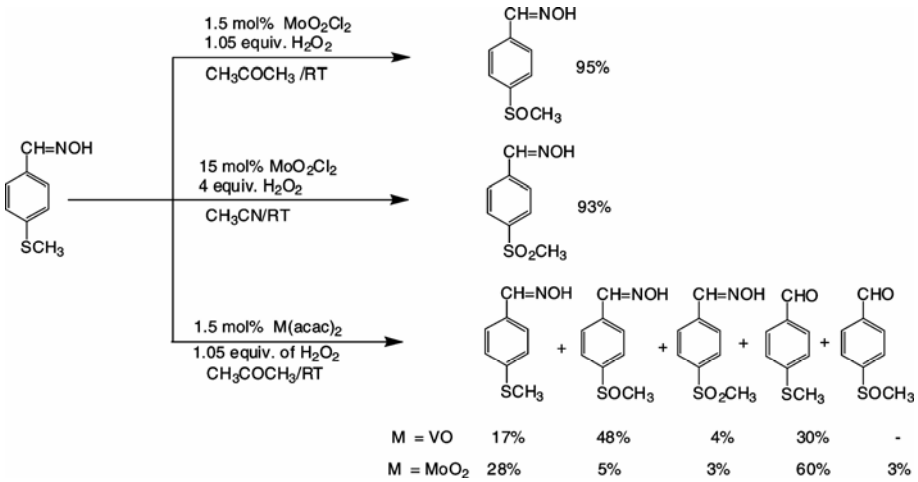
Condition (**A**): MoO_2Cl_2 (1·5 mol%), 30% H_2O_2 (1·05 equiv.), acetone: water (1·5:1, v/v), RT.

Condition (**B**): MoO_2Cl_2 (15 mol%), 30% H_2O_2 (4 equiv.), acetonitrile, RT.

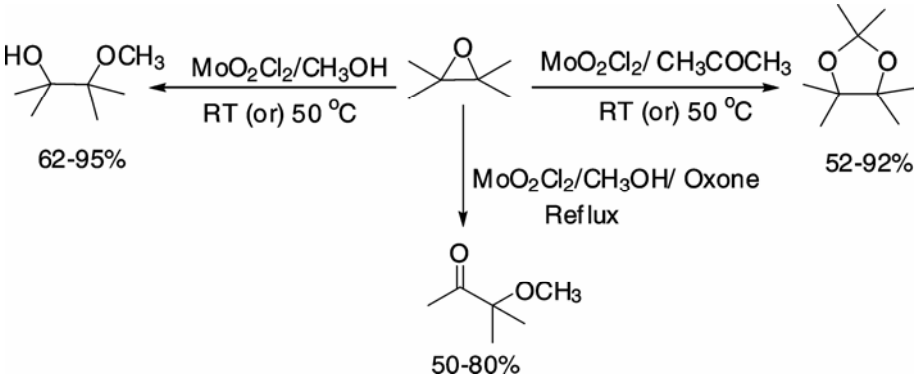
Scheme 24. Oxidation of sulfides to sulfoxides and sulfones with MoO_2Cl_2.

2.2l *Selective and controlled oxidation of sulfides to sulfoxides and sulfones:* Selective and controlled oxidation of sulfides to sulfoxides and sulfones is achieved by H_2O_2 using MoO_2Cl_2 as the catalyst (scheme 24).[43] Substituted and unsubstituted aryl–alkyl, diaryl, benzyl–alkyl and dialkyl sulfides were successfully and selectively oxidized to the corresponding sulfoxides and sulfones in high yields.

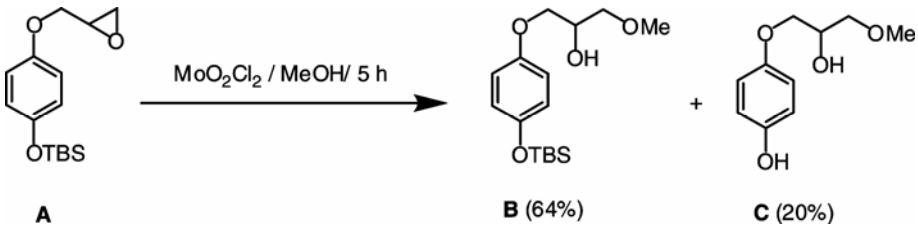
Sulfides with additional functionalities susceptible to oxidation or deprotection such as alkenes, alkynes, alcohols, esters, aldehydes and oximes were found to yield sulfoxides and sulfones without



Scheme 25. Selective oxidation of 4-(methythio)benzaldehyde oxime with various catalysts.



Scheme 26. Conversion of the various epoxides to β-methoxy alcohols, acetonides and α-methoxy ketones.



Scheme 27. Methanolysis of *tert*-butyldimethylsilyl (TBS) protected epoxide.

affecting the sensitive functional groups. For example, no epoxidation was observed during the oxidation of allyl phenyl sulfide although molybdenum complexes are well known for epoxidation. Moreover, alcohol oxidation does not occur as seen in the case of 3-(phenylthio)propanol and 4-(methylthio)benzyl alcohol. The sulfide containing aldehyde functionality did not show formation of carboxylic acids. Since oxime functional groups will undergo oxidative deprotection with oxidative condition, author has examined the oxidation of 4-(methylthio)benzaldoxime which contains sulfide as well as oxime functionalities (scheme 25).[43]

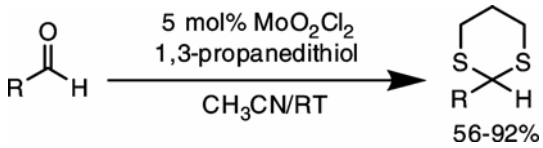
MoO_2Cl_2/H_2O_2 system shows clear-cut stability of oximes while selectively oxidizing the sulfide to sulfoxide and sulfone. It is important to note that other similar oxidants such as $VO(acac)_2/H_2O_2$, $MoO_2(acac)_2/H_2O_2$ gave a mixture of products while oxidizing 4-(methylthio)benzaldoxime (scheme 25).[43]

2.2m *Ring opening reactions of epoxides:* MoO_2Cl_2 was used as an efficient catalyst for the conversion of the epoxides to β-methoxy alcohols, acetonides and α-methoxy ketones under optimized reaction conditions (scheme 26).[44]

Methanolysis of various epoxides were carried out using 5 mol% of MoO_2Cl_2 in methanol. Simple epoxides like styrene oxide, cyclohexene oxide undergo ring opening reaction with methanol to provide 2-methoxy phenyl ethanol and 2-methoxy cyclohexanol respectively, in quantitative yields at room temperature. In the case of other unsymmetrical epoxides, we observed the nucleophile attack at less hindered side of the epoxides which gave regioselective products at room temperature or 50°C. The potential benefits of this methodology were examined with some sensitive functional groups like phenol, alcohol, aldehyde and oximes, where no self ring opening polymerization, deprotection or rearrangement was observed. Allyl, propargyl, benzyl and tosyl protected epoxides gave the desired products in good yields. In the case of *tert*-butyldimethylsilyl (TBS) protected epoxide **A**, the expected product was obtained as a major product **B** in 64% along with the deprotected product **C** in 20% (scheme 27).

The acetonidation reactions were carried out using 5 mol% of MoO_2Cl_2 in acetone at room temperature or 50°C. During the reactions of various epoxides, functional groups such as alcohol, aldehyde, oxime, allyl, propargyl, benzyl and tosyl, were compatible under the conditions employed in this study. In the case of TBS protected epoxide, desired protect was obtained in high yield (85%) along with small amount of deprotected product (5%).

It is also interesting to note that direct conversion of epoxides to α-methoxy ketones were obtained using 15 mol% of MoO_2Cl_2 with 1·1 equivalent of oxone ($KHSO_5$) in methanol under reflux conditions (scheme 26). Cyclohexe oxide, allyl, propargyl, tosyl, benzyl protected and long chain epoxides were converted to corresponding methoxy ketones in good yields. Other epoxides which contain sensitive func-



Scheme 29. Thioacetalization of aldehydes using MoO_2Cl_2.

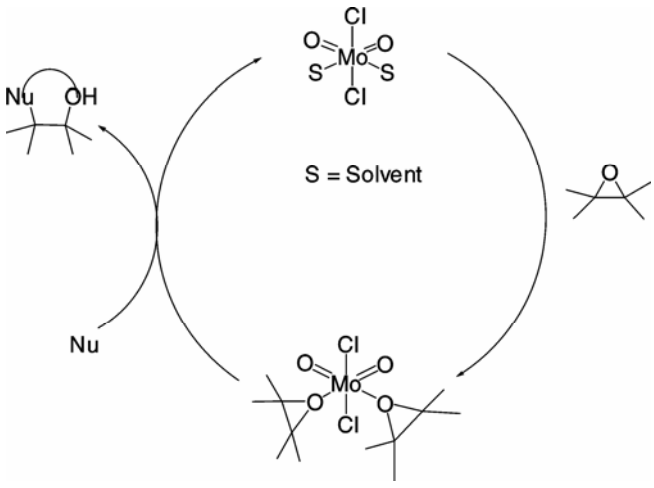
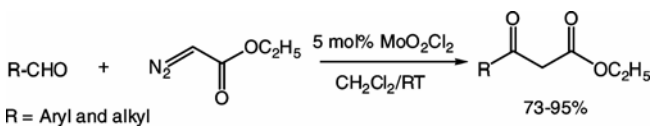


Figure 10. Proposed mechanism for epoxide ring opening reaction.



Scheme 28. Condensation of aldehydes with ethyl diazoacetate.

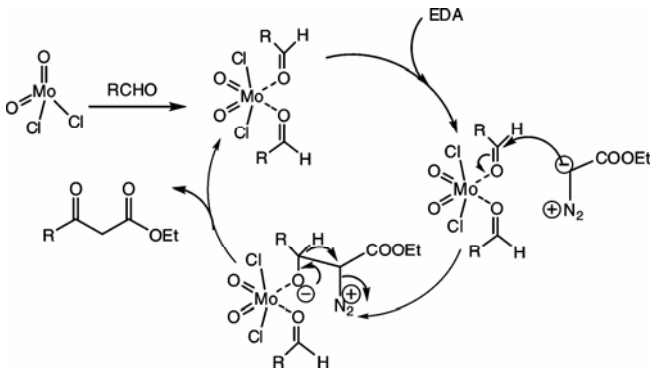


Figure 11. Proposed mechanism for the synthesis of β-keto esters.

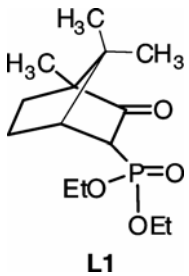
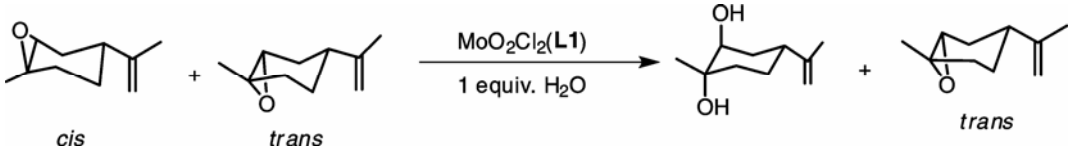


Figure 12. Structure of the ligand **L1** (where camphor moiety is in (+) configuration).



Scheme 30. Diastereoselective ring opening of limonene oxide with water using MoO_2Cl_2 (**L1**).

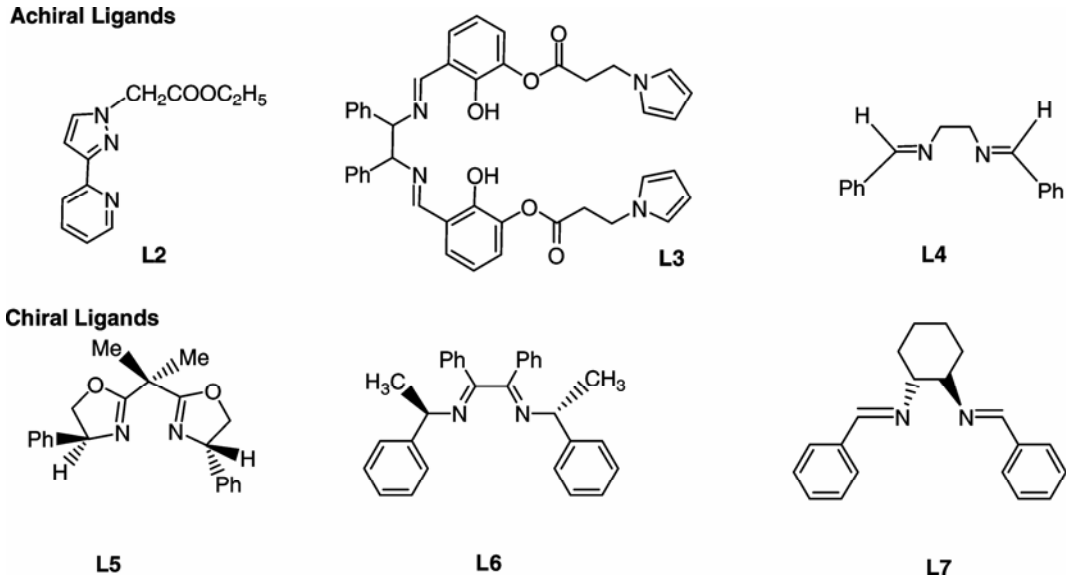


Figure 13. The bidentate chiral and achiral ligands used for complexation with MoO_2Cl_2 to generate MoO_2Cl_2 (**L**).

tional groups such as phenol, alcohol, aldehyde, oxime and TBS were not tolerated during this conversion.

The proposed mechanism for epoxide ring opening is shown in figure 10. It is well known that MoO_2Cl_2 can bind with various kinds of oxygen donors to give corresponding molybdenum addition compounds. The first step presumably involves the coordination of epoxide to the vacant sites of MoO_2Cl_2. In the next step possibly the nucleophlie attacks the epoxide which gives the desired products.

2.2n *Synthesis of β-keto esters:* MoO_2Cl_2 was utilized as the catalyst for the synthesis of β-keto esters by condensing various aldehydes with ethyl diazoacetate (scheme 28).[45] The reactions were carried out using 5 mol% of MoO_2Cl_2 in the presence of 1·2 equivalent of ethyl diazoacetate at room temperature in dichloromethane. Aromatic, aliphatic and heterocyclic aldehydes are successfully condensed with ethyl diazoacetate to obtain corresponding β-keto esters in high yields.

The proposed mechanism for the synthesis of β-keto esters is shown in figure 11. The reaction probably proceeds through the activation of the aldehyde by complexation with molybdenum (VI) dichloride dioxide. The carbon nucleophile attacks on the carbonyl group aldehyde and subsequent 1,2-hydride shift with loss of N_2 resulting in the formation of β-keto ester (figure 11).

2.2o *Thioacetalization of aldehydes:* MoO_2Cl_2 was used as a novel catalyst for the thioacetalization of heterocyclic, aromatic and aliphatic aldehydes to the corresponding dithianes with 1,3-propanedithiol (scheme 29).[46] The reactions were carried out at room temperature in acetonitrile using 5 mol% of the catalysts to obtain moderate to excellent yields. The author also claimed that $MoCl_5$ also works in similar manner like MoO_2Cl_2.

2.2p *Applications of various complexes of MoO_2Cl_2:* Several complexes of general formula MoO_2Cl_2(**L**) (figure 2) are prepared from MoO_2Cl_2 and a range of bidentate ligands (figures 12 and 13). These com-

plexes are used as catalysts for some organic transformations as described in this section.

For example, diastereoselective ring opening of limonene oxide was studied with catalytic amount of MoO_2Cl_2(**L1**) (where **L1** is a ketophosphonate derived from camphor, figure 12).[47] The selective ring opening of *cis* (±)-limonene oxide is initiated by water to give the *trans*-diaxial diol. The *trans* isomer of the limonene oxide remains almost completely unreacted, thus providing a method for the kinetic separation of the trans diastereomer (scheme 30).

In addition to this report, various MoO_2Cl_2-based achiral complexes MoO_2Cl_2(**L2**),[48] MoO_2Cl_2(**L3**),[49] MoO_2Cl_2(**L4**),[50] etc. and chiral complexes MoO_2Cl_2(**L5**),[51] MoO_2Cl_2(**L6**),[52] MoO_2Cl_2(**L7**),[52] etc. were synthesized using appropriate ligands (figure 13). The catalytic properties were studied for these complexes by epoxidation of olefins, where reactions were carried out at 55°C using 1 mol% of complexes with *tert*-butyl hydrogen peroxide in decane. During the epoxidation of olefins with chiral molybdenum complexes, less than 10% of enantiomeric excess (*ee*) were observed.

3. Conclusions

This review focused on the role of MoO_2Cl_2 in a variety of organic transformations published till mid-2008. This *cis*-dioxo molybdenum compound is commercially available and has already shown potential to catalyse a range of reactions. Sensitive functional groups are tolerated during the catalysis steps in presence of this mild and selective catalyst. Thus, MoO_2Cl_2 is promising for possible applications as a catalyst during multi-step synthesis. As the catalyst is not yet well explored, more applications in organic synthesis are highly expected during coming years.

Acknowledgements

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