

Dioxomolybdenum reagents in organic synthesis: utility of redox capability to design reduction and oxidation

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Abstract | The usefulness of dioxomolybdenum reagents in oxo-transfer reactions have been reviewed. The redox ability of dioxomolybdenum reagent has been utilized in designing several synthetic methods, which are useful in organic synthesis. Several reactions such as oxidation of alcohols, sulfides, amines, azides olefins etc are accomplished by using dioxomolybdenum reagents. Similarly, it is also demonstrated that dioxomolybdenum complex is useful in performing reduction of aldehydes, ketones, esters, azides etc. A fine tuning of reaction conditions provides suitable conditions to perform either oxidation or reduction by using catalytic amount of reagents. The oxidation reactions are further simplified by employing the polymer supported molybdenum reagents.

Introduction

Redox reactions are fundamental in chemistry, which help in understanding the reactivity of several enzymatic reactions that occur in nature. Mother Nature has designed several reactions, ranging from simple to more complicated, in aqueous medium. A careful look at these reactions reveals the importance of redox chemistry associated with these reactions. Therefore, mimicking nature is one of the unfulfilled dreams of chemists and the attempts in this direction have resulted in several useful reactions. Amazingly, the energy metabolism is based on the redox reactions. Indeed the redox biochemistry of organisms and enzymes has transformed the environment slowly and steadily. Anoxygenic bacterial photosynthesis is coupled with redox chemistry of sulfur compounds (such as hydrogen sulfide, sulfur or thiosulfate), hydrogen, or organic acids to solar energy to power metabolism. Nitrogen fixation turns out to be one of the

important events in evolution, which has resulted in the formation of amino acids. Nitrogen fixation turned out to be a major event in evolution process, which has transformed inert nitrogen to biologically available form. Designing redox reaction may result in reactions with a good atom economy and clean reaction under green conditions. The present review is presenting some of the redox reactions associated with dioxomolybdenum complexes. A fine tuning of reaction conditions allows to perform the reactions in opposite directions and few reactions are more effective in water.

Chemistry of metal-oxo compounds is a well explored area, which has implications in chemistry and biology.¹ Therefore, studies on various transition metal oxides have produced a variety of transformations, which are useful in academia as well as in industries.² The transition metals such as Mo, V, Cu, W etc. are capable of existing in multiple oxidation states. These

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metals, when found together with different donor atoms such as P, S, N and O exhibit numerous redox possibilities. Due to this unique feature many novel inorganic and bioinorganic chemistry have been reported in the literature.³ Among the numerous transition metal-oxo compounds, the chemistry of molybdenum compounds is profoundly explored area, which has been producing a variety of useful chemical transformations in organic synthesis.^{1b, 4} Apart from this, research work on dioxo-molybdenum compounds has also led to the discoveries which are relevant to enzyme action due to their structural and functional similarities with several molybdoenzymes.⁵

Biological significance

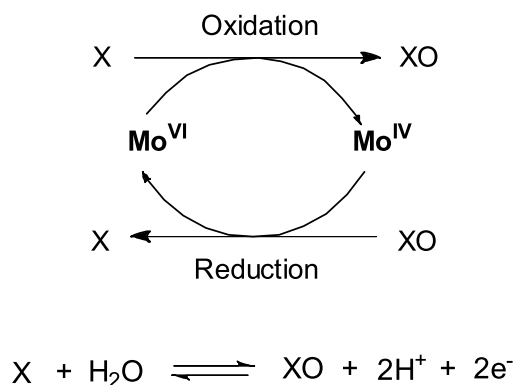
Molybdenum is an essential constituent of various molybdoenzymes such as nitrogenase, xanthine oxidase, dehydrogenase, sulfite oxidase and nitrate reductase.^{1f, 6} Therefore, the functional and structural mimic of Mo containing enzymes have been the study of interest of various research groups.^{5, 7} Molybdenum containing enzymes are extensively distributed in nature and participate in catalytic cycles of a variety of biological reactions.⁸ Crystallographic and X-ray studies have revealed that, mononuclear molybdenum (IV) or (VI) is present in the active sites of several enzymes. Interestingly, it is also found that the molybdenum in these enzymes is coordinated by

sulfur donor ligands.⁹ In this perspective, the studies on molybdenum compounds have led to better insight in understanding the structure and functions of various molybdoenzymes.⁵ Molybdoenzymes such as xanthine oxidase, dehydrogenase, sulfite oxidase and nitrate reductase are known to catalyze a variety of two electron redox reactions involving a net exchange of an oxygen atom between the Mo-enzymes and substrates. This typical catalytic oxidation/reduction cycle is presented in Scheme 1.

In a catalytic cycle involving molybdenum centre, $\text{Mo}^{\text{VI}}\text{O}_2$ and $\text{Mo}^{\text{IV}}\text{O}$ intermediates are considered as active species involved in redox reactions carried out by several molybdoenzymes.¹⁰ Xanthine oxidase catalyzes oxidative hydroxylation of purines and pyridines including conversion of hypoxanthine to xanthine and xanthine to uric acid.^{1e, 11} Interestingly, this transformation occurs in the presence of molecular oxygen under biochemical conditions (Scheme 2). Aldehyde oxidase oxidizes purines, pyrimidines, pteridines and is involved in nicotinic acid metabolism.

Most of these molybdoenzymes contain thiometalates that stabilize the metal centre by coordinating through pairs of sulfur atoms in active site and these sulfur atoms play a significant role in facilitating the enzyme reactions.¹² In this perspective, a large amount of work has been accomplished to examine the ability of dioxo-molybdenum complexes to serve as functional and structural model of these oxo-transfer molybdoenzymes.^{5, 13}

Scheme 1: Catalytic redox cycle for molybdo-enzymes.



Scheme 2: Oxidation reactions catalyzed by xanthine oxidase.

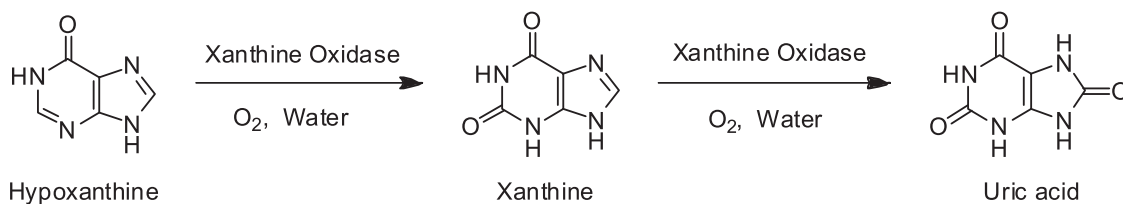
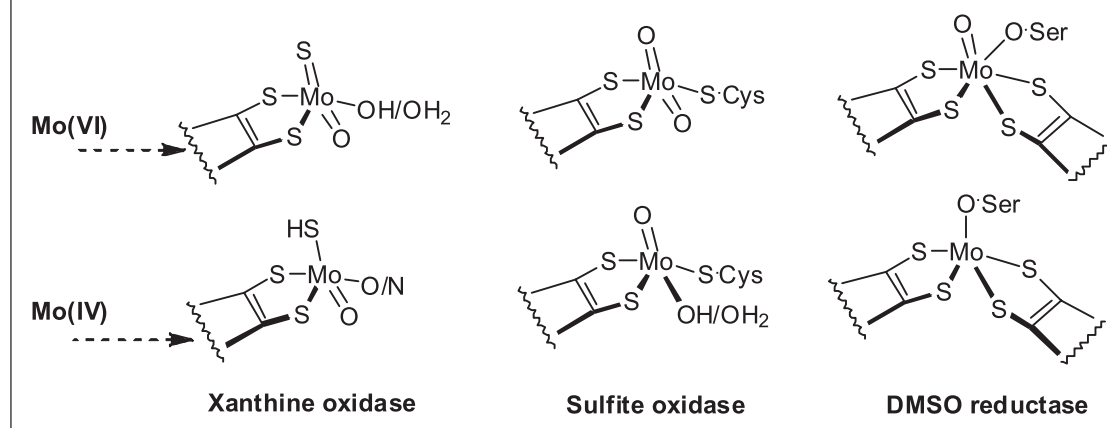


Figure 1: Active site structures of molybdo-enzymes.



Molybdenum reagents

Figure 1 presents active site of few molybdo-enzymes.^{5a} Some of the key features that are present in these molybdoenzymes are as follows. These enzymes contain sulfur atoms as bidentate ligands, which are coordinated to metal centers. Most of the oxo-transfer molybdenum reagents contain sterically demanding sulfur ligands, thereby making them suitable models for molybdoenzymes.

The literature survey indicates that dialkyldithiocarbamate complex of molybdenum (VI as well as IV) appears to possess these features. Several reagents such as molybdenum (VI) dioxo-bisdiethyldithiocarbamate (**1**, $\text{MoO}_2(\text{Et}_2\text{NCS}_2)_2$), $\text{MoO}_2(\text{acac})_2$, sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) and ammonium molybdate [$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$] were also screened under a variety of reaction conditions.

Oxo-transfer reactions of molybdenum dioxo-bisdiethyldithiocarbamate

Oxidation is one of the fundamental methods for introducing and manipulation of organic functional groups. Interestingly, the development of new methods is sought after despite the availability of several oxidizing agents. Furthermore, most of the conventional methods of oxidation utilize the stoichiometric amount of reagents thereby making these methods less attractive.¹⁴ Additionally, there is a need for selective oxidation protocols preferably under eco-friendly conditions. Therefore, there are several attempts in this direction in developing environmentally benign oxidation strategies by employing catalytic amount of reagents in the presence of molecular oxygen or hydrogen peroxide in aqueous medium. Furthermore, the oxidation of alcohols^{1c} by metal-oxo complexes is a well known reaction, especially by using Cr(VI) and Mn(VII)

complexes.¹⁵ Molybdenum complexes catalyzed oxo-transfer reactions have gained considerable importance due to their relevance in biological processes and most importantly, molybdenum is much less toxic than many other metals of industrial importance.¹⁶

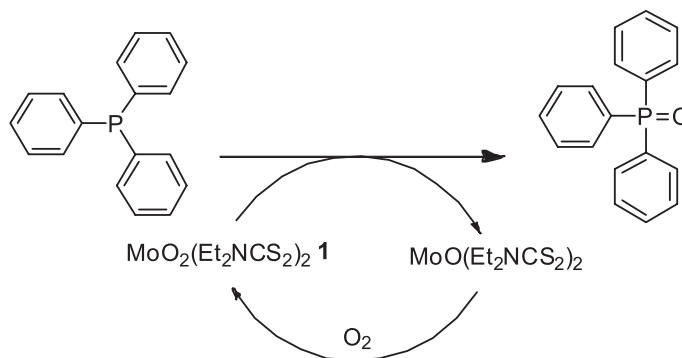
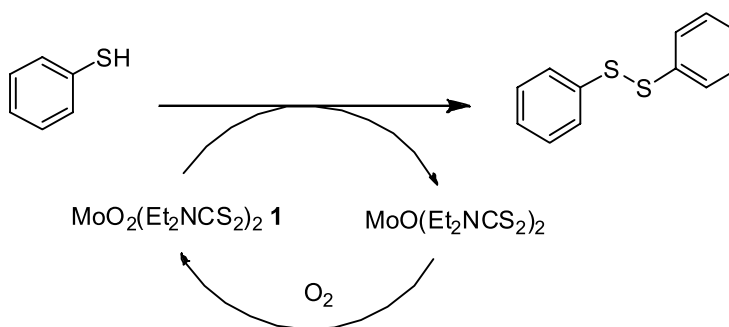
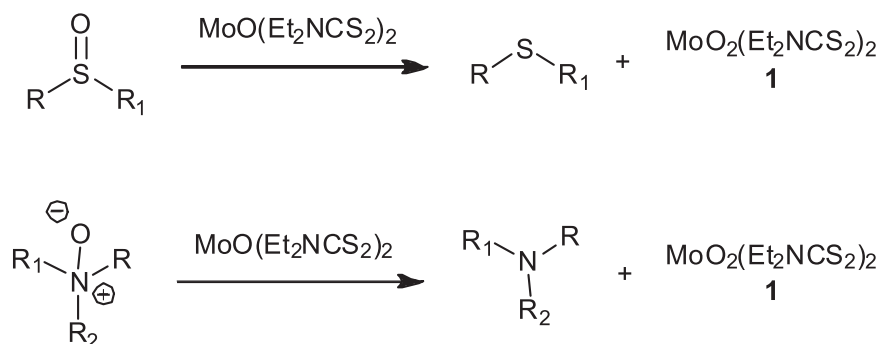
A cursory glance at the literature on molybdenum dioxo-bisdiethyldithiocarbamate (**1**) reveals that there are several attempts to conceive the reagent **1** as an oxo-transfer reagent either in catalytic amount or in stoichiometric amounts. Apart from this, the structural and functional mimic of oxo-molybdoenzymes is one of the well addressed fields of investigation.^{5,7}

The first report on oxygen transfer reaction catalyzed by **1** was documented by Barral¹⁷ and co-workers in 1972. In their preliminary studies, a catalytic oxidation cycle for triphenyl phosphines in presence of molecular oxygen is reported (Scheme 3).

Later on, Holm¹² and co-workers reported the oxidations of various thiols to corresponding disulfides catalyzed by **1** as shown in Scheme 4.

Interestingly, Mitchell,^{7a} in 1975 has documented the first example of oxygen transfer from various organic oxides to Mo(IV) system such as $\text{MoO}(\text{Et}_2\text{NCS}_2)_2$ as shown in Scheme 5. In this stoichiometric reaction, Mo(IV) was oxidized to Mo(VI) by sulfoxides and N-oxides to produce the corresponding sulfides and amines respectively. It is also interesting to note that sulfoxides and N-oxides are also reduced to the corresponding sulfides and amines by crude extracts containing molybdoenzymes.¹⁸

Epoxidation reactions catalyzed by molybdenum (VI) reagent with alkyl hydroperoxides are well known in the literature.¹⁹ However in 1988 Moloy¹⁵ has reported that the epoxidation of olefin by

Scheme 3: Oxo-transfer reaction catalyzed by molybdenum (VI) dioxo-bisdiethyldithiocarbamate.**Scheme 4: Oxidation of thiol catalyzed by molybdenum (VI) dioxo-bisdiethyldithiocarbamate.****Scheme 5: Molybdenum (IV) dioxo-bisdiethyldithiocarbamate mediated oxo-abstraction reactions.**

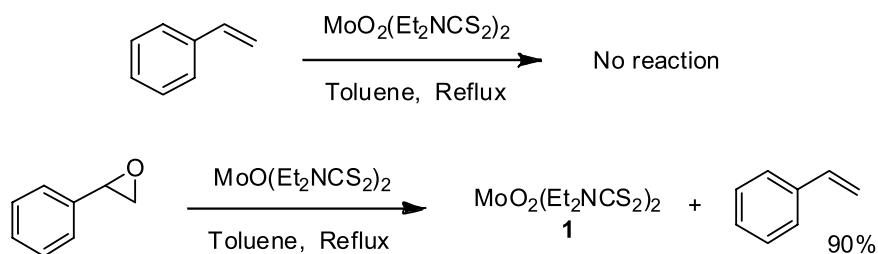
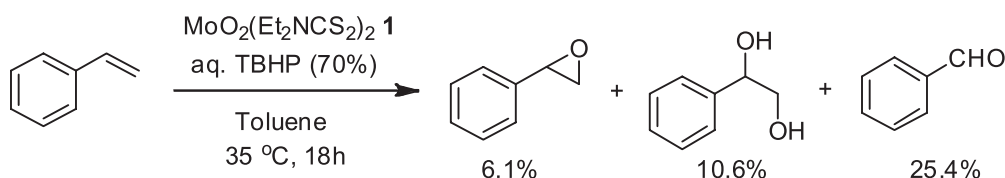
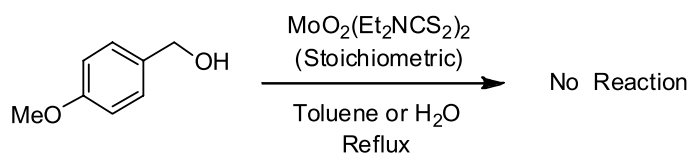
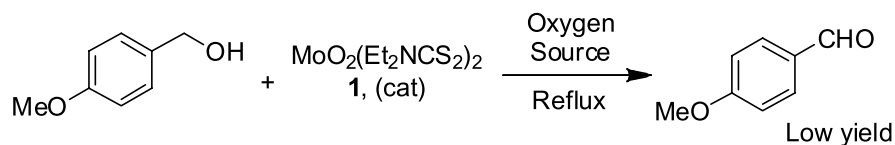
molybdenum dioxo-bisdiethyldithiocarbamate **1** is an unfavorable reaction even under the forcing reaction conditions such as high temperatures, high pressure and long reaction time. On the other hand, he has demonstrated that the deoxygenation of epoxide by Mo(IV) analogue of **1** [$\text{MoO}(\text{Et}_2\text{NCS}_2)_2$] is a favorable process to produce the corresponding olefin and **1** in good yields as shown in Scheme 6.

Interestingly, Gomez and coworkers²⁰ have reported the oxidation of olefins catalyzed by molybdenum dioxo-bisdiethyldithiocarbamate **1** in presence of aq. TBHP to produce a small amount

of epoxide along with the corresponding aldehyde and diol (Scheme 7).

Oxidation reactions catalyzed by molybdenum dioxo-bisdiethyldithiocarbamate

Although several molybdenum complexes have been studied as models in heterogeneous catalysis, the utility of molybdenum dioxo-bisdiethyldithiocarbamate **1** as an effective catalyst is limited to the oxidation of trialkyl phosphine and thiols.^{12,17} Several attempts to develop molybdenum dioxo-bisdiethyldithiocarbamate **1** as catalyst for oxo-transfer reactions have

Scheme 6: Oxo-abstraction reaction by using molybdenum (IV) dioxo-bisdiethyldithiocarbamate.**Scheme 7: Oxidations catalyzed by molybdenum (VI) dioxo-bisdiethyldithiocarbamate.****Scheme 8: Oxidation of alcohol catalyzed by molybdenum dioxo-bisdiethyldithiocarbamate.****Scheme 9: Oxidation of alcohol in presence of various oxygen sources.**

OxygenSource: NMMO, mCPBA, O₂aq, H₂O₂aq, TBHP

met with limited success. Additionally, several molybdoenzymes are known to bind to nitrogen and acetylene.²¹

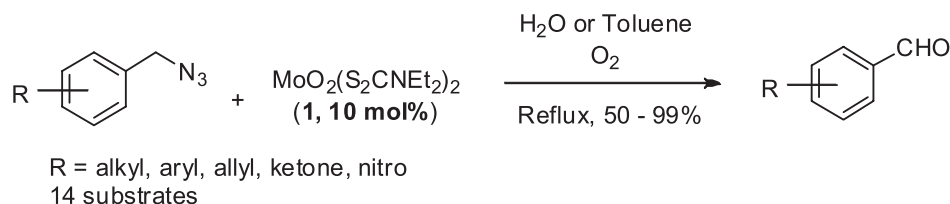
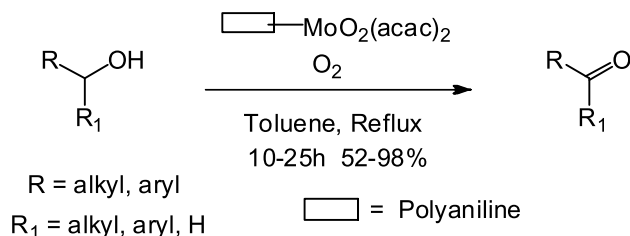
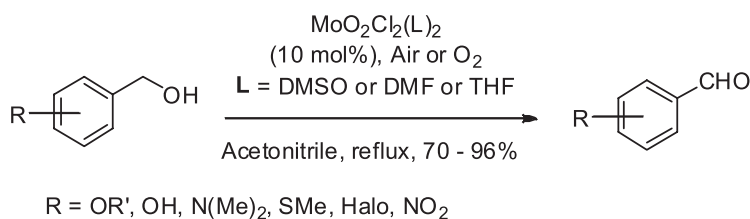
Oxidation of alcohols

Oxidation of alcohols to aldehydes and ketones is a fundamental functional group transformation in organic chemistry, and numerous reagents have been developed to accomplish this transformation.²² There are several reports on the utility of Mo(VI) complexes for oxidation of alcohols to the corresponding carbonyl compounds. However, oxidation of alcohols to produce carbonyl compounds by using reagent **1** is not known in the literature. The preliminary reaction of stoichiometric amount of reagent **1** with *p*-methoxybenzyl alcohol was unsuccessful in producing the oxidized product (Scheme 8).

The oxidation of *p*-methoxybenzyl alcohol by **1** in the presence of NMMO, *m*-CPBA and molecular oxygen (O₂) failed to oxidize alcohols (Scheme 9). The reaction of *p*-methoxybenzyl alcohol with **1** (10 mol %) in the presence of aq. H₂O₂ (30%) produced the corresponding aldehyde in 5% yield. A prolonged reaction of *p*-methoxybenzyl alcohol with **1** and aq. TBHP (70%) has produced the corresponding aldehyde in 10%–30% yields.²³

Oxidation of azides

A catalytic cycle of aerobic conversion of benzylic azides to the corresponding aldehydes by using catalytic amount of reagent **1** under aqueous conditions is presented in Scheme 10.²⁴ The oxidation of benzylic azide catalyzed by **1** is highly chemoselective and provides an opportunity to

Scheme 10: Catalytic oxidation of various benzylic azides in presence of molecular oxygen.**Scheme 11: Oxidation catalyzed by polyaniline supported molybdenum reagent.****Scheme 12: Oxidation of alcohols catalyzed by MoO₂Cl₂(L)₂.**

synthesize aldehydes in the presence of several functional groups such as alcohols, chlorides, olefins, esters and ketones. More importantly, the oxidation of azides stops at corresponding aldehyde stage, without further oxidation to the corresponding carboxylic acids. Furthermore, the preliminary studies show that the oxygen is transferred from molecular oxygen and not from the solvent water.

Punniyamurthy²⁵ and coworkers reported an aerobic oxidation of alcohols by using the catalytic amount of polyaniline supported MoO₂(acac)₂ complex in molecular oxygen atmosphere. Various alcohols were efficiently oxidized to carbonyl compounds in toluene at reflux temperatures in moderate to good yields (Scheme 11). Interestingly, the polymer supported molybdenum catalyst can be recycled without much loss of its activity. Authors have pointed out that, the oxidation of primary alcohols stops at aldehyde stage and do not undergo further oxidation to carboxylic acids. In these oxidations, reaction of primary alcohols is faster than the secondary alcohols.

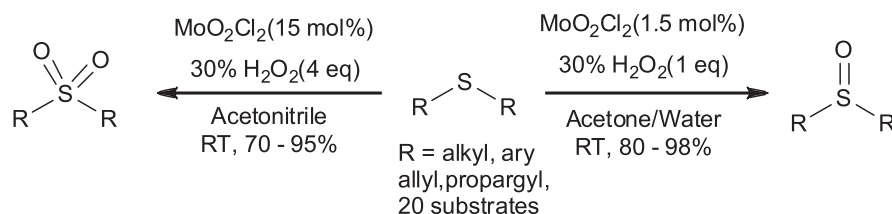
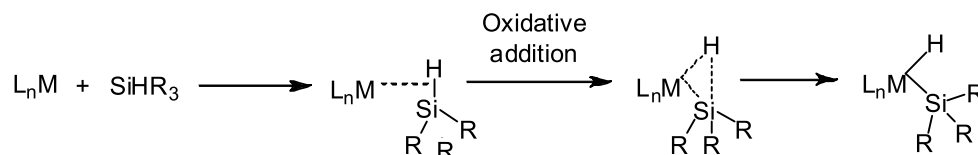
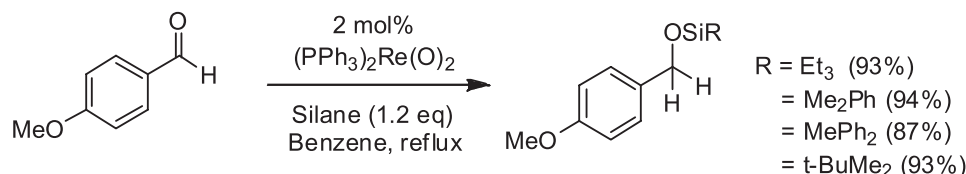
Recently, Chand²⁶ and coworkers have reported the selective and controlled aerobic oxidation of benzylic alcohol derivatives to the corresponding

carbonyl compounds in refluxing CH₃CN using catalytic amounts of MoO₂Cl₂(L)₂ where L is DMSO, DMF or THF (Scheme 12). Various activated and inactivated benzylic alcohols were oxidized under open air without using any other external co-oxidants. In order to sustain the catalytic oxidations, the authors have performed the bubbling of molecular oxygen in to the reaction mixture.

It is demonstrated that the selective oxidation²⁷ of sulfides to sulfoxides and sulfones by using H₂O₂ and commercially available MoO₂Cl₂ as the catalyst system in good yields (Scheme 13). A variety of sulfides is smoothly oxidized without affecting other groups such as alkyl, methoxy, olefin, alkyne, ester, aldehyde, alcohols, nitro etc in aqueous medium.

Reduction reactions using molybdenum reagents

Transition metal complexes with metal–oxygen multiple bonds are well known catalysts for oxidation and oxo-transfer reactions.²⁸ These classes of metal complexes are known for their unique redox capabilities. However, their utility in organic transformations, particularly in reductions of organic functional groups is rare.^{28, 29} Additionally,

Scheme 13: Oxidation of sulfides catalyzed by MoO₂Cl₂(L)₂.**Scheme 14: Activation of Si-H bond.****Scheme 15: Hydrosilylation of aldehydes.**

several traditional metal catalysts, which are capable of exhibiting redox reactions are sensitive to air and moisture. Functional group incompatibility is another major drawback, which limits the utility of such reagents.^{28a,30} Therefore, there is a necessity to develop synthetically useful reagents for such catalytic reactions.²⁸ This part of the review presents some of the reduction reactions developed by using molybdenum reagents.

Biological significance of azide reduction

Nitrogenase, a molybdenum-containing enzyme is known to reduce azide ion to the corresponding amine and dinitrogen.³¹ It has been postulated that Mo-S clusters may be responsible for this reduction of azides. In this context, we thought it is relevant to study the reactivity molybdenum dioxobisdiethyldithiocarbamate **1**, with organic azides. Due to our success in utilizing molybdenum dioxobisdiethyldithiocarbamate (**1**) for the oxidations of various azides²⁴ and alcohols,³² we turned our attention to explore the efficiency of catalyst **1**, particularly as reducing agent.

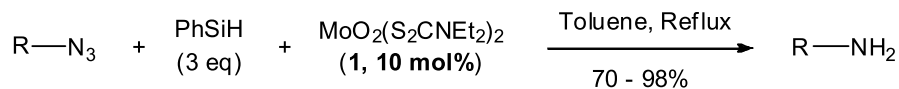
Catalytic transfer of hydrogen

Catalytic transfer of hydrogen (CTH) is a widely accepted alternative method, which does not require the use of hydrogen gas for the reduction in organic

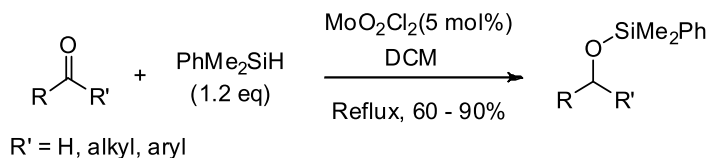
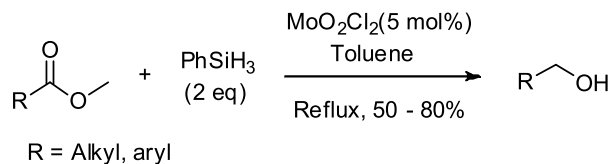
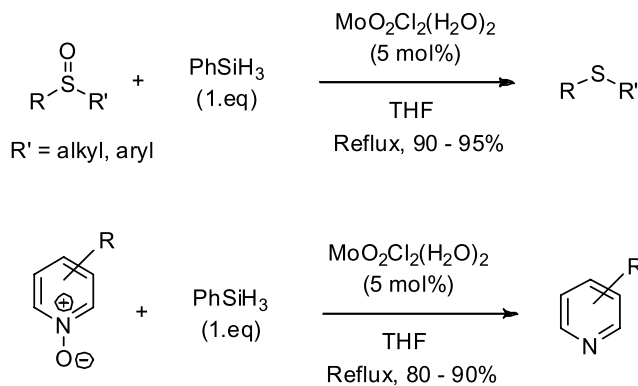
synthesis.³³ The activation of Si-H bond by several metals is a newly established method for the catalytic transfer of hydrogen in reduction process. It is recently documented by Wilking and co-workers that the addition of Si-H bond to metal carrying a ligand π -bond results in the activation of Si-H bond via oxidative addition³⁴ by means of formation of metal hydride³⁵ species (Scheme 14). Interestingly, this process of adding Si-H bond across the metal-ligand π -bond converts strongly oxidizing M=O complex to silyloxy substituted metal hydride, which could potentially be employed as a reducing agent.

This concept has been employed by Toste³⁶ and coworkers in hydrosilylation of aldehydes by using rhenium (V) dioxo complex with various silanes to produce the corresponding trialkylsilyl ethers as shown in Scheme 15.

A catalytic amount of molybdenum dioxobisdiethyldithiocarbamate (**1**, MoO₂[S₂CNET₂]₂) with PhSiH₃ is an effective catalyst for the reduction of azides to the corresponding amines.³⁷ This reduction of azides by **1**, was inspired by the reductive silylation of aldehydes through the activation of silanes.³⁸ This reduction tolerates a variety of reducible functional groups such as olefin, aldehydes, ketones, esters, amides and ethers, acetals etc. This strategy was also extended to various aliphatic azides to synthesize amine and

Scheme 16: Reduction of azides to amines.

R = CHO, Ketone, ester, nitro, cyano, olefine
amide, alkyl, aryl etc

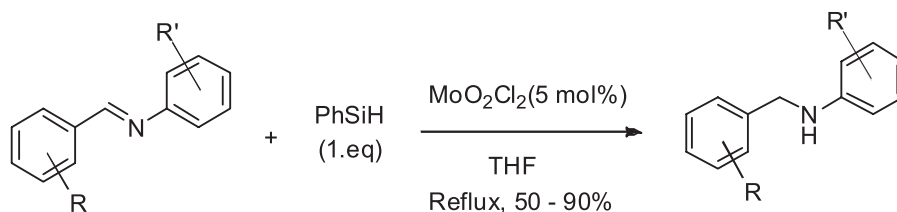
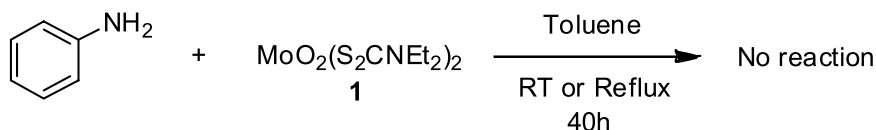
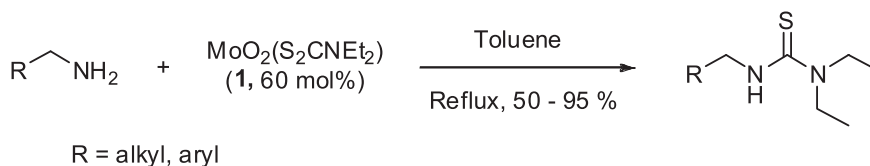
Scheme 17: Reduction silylation of aldehydes using molybdenum complex.**Scheme 18: Reduction of esters by using molybdenum complex.****Scheme 19: Reduction of sulfoxides and pyridine N-oxides.**

their N-Boc derivatives in good yields. Scheme 16 illustrates few examples. The scope of this reduction was studied extensively with several functionalized azides. Several azides with a variety of functional groups underwent smooth reduction to furnish the corresponding amines in good to excellent yields.

The concept of catalytic transfer of hydrogen (via activation of Si-H bond) was also demonstrated by Royo³⁹ and co-workers for the reductive silylation of aldehydes using molybdenum complex. The high valent dioxo-molybdenum complex (MoO_2Cl_2) catalyzes the addition of dimethylphenylsilane to a variety of carbonyl compounds to afford the corresponding dimethylphenylsilyl ethers in quantitative yield as shown in the below Scheme 17.

Fernandes⁴⁰ and co-workers have reduced a variety of ester to the corresponding alcohols by employing the concept of silane activation. They have developed $\text{MoO}_2\text{Cl}_2/\text{PhSiH}_3$ as an effective catalyst system for the reduction of aliphatic and aromatic esters to the corresponding alcohols in good yields (Scheme 18).

Recently, a novel method for the reduction⁴¹ of sulfoxides and pyridine N-oxides using phenylsilane was observed by Fernandes research group (Scheme 19). Authors have employed a catalytic amount of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ complex for the reduction of sulfoxides and N-oxides in excellent yields. A wide variety of functional groups were

Scheme 20: Reduction of imines.**Scheme 21: Oxidation of aniline by using molybdenum dioxo-bisdiethyldithiocarbamate.****Scheme 22: Transfer of ligand from molybdenum dioxo-bisdiethyldithiocarbamate.**

unaffected during the reductions. A green protocol for this reaction was developed in water with the air-stable catalytic system PMHS/MoO₂Cl₂(H₂O)₂.

A novel catalytic system, MoO₂Cl₂/PhSiH₃, for the reduction of imines⁴² in excellent to moderate yields was developed by Fernandes and co-workers (Scheme 20). They have reduced various imines selectively in the presence of functional groups such as fluoro, nitro and esters.

Catalytic oxo-transfer reactions involving the reaction of an oxygen donor with organic substrates in the presence of a transition metal catalyst holds considerable promise in oxidation reactions.⁴³ In this context, several metals, and their derivatives were exploited for the catalytic oxidations of amines.⁴⁴ Oxidation of amines is a reaction of significant importance with implications in biology, medicine and synthetic chemistry.⁴⁵ Selective and catalytic oxidations of aliphatic amines are usually difficult than the aromatic amines. Additionally, metal-catalyzed oxidation of amines is of interest due to its relevance in enzymatic degradation in biological systems.⁴⁶ Their utility in liquid crystals is well known.⁴⁷ Although, a variety of oxo-molybdenum complexes are known for the oxidation of organic compounds,⁴⁸ their utility in transferring oxygen to primary amines is not well-known.

Interestingly, the molybdenum (IV) dioxo-bisdiethyldithiocarbamate [MoO(Et₂NCS₂)₂], at

lower oxidation state is known to deoxygenate⁴⁹ sulfoxides and N-oxides to furnish the corresponding molybdenum (VI) reagent **1** as shown in Scheme 5.

Ligand transfer reactions

There are several reports on the utility of Mo(VI) reagents in oxidation of amines (Scheme 22).^{35–37,42} However, there are no reports on the utility of molybdenum dioxo-bisdiethyldithiocarbamate (**1**) to oxidize primary amines.

This reaction of benzyl amine with **1**, clearly took a different course *i.e.* instead of oxygen transfer from the reagent to the substrate, there was transfer of sulfur and nitrogen (ligand) from the reagent **1** to benzyl amine,^{50,51} to produce the corresponding trisubstituted thiourea derivative^{52,53} (Scheme 22).

Conclusion

This review has presented a brief account of several attempts to uncover the utility of dioxomolybdenum complexes. The redox capability of dioxomolybdenum complexes has been well exploited in designing several useful methods in organic synthesis. A systematic investigation by various groups has revealed several useful methods. Additionally, it was also found that in a forcing reaction conditions, some of the dioxomolybdenum reagent would transfer the ligands instead of oxygen.

Apart from these observations, some of the reactions found to proceed only in water.

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