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Molybdenum reagents

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Abstract

Some of the key features that are present in these molybdoenzymes are as follows. These enzymes contain sulfur atoms as follows. These enzymes contain sulfur atoms as bidentate ligands, which are coordinated to metal centers. Most of the oxo-transfer molybdenum reagents contain dtatically demanding sulfur ligands, therby making them suitable models for molybdoenzymes. The literature survey indicates that dialkylidithiocarbamate complex of molybdenum (VI as well as IV) appears to posses these features. Several reagents such as molybdenum (VI) dioxobisdiethylidithiocarbamate (1, $\text{MoO}_2\text{Et}_2\text{NCS}_2$), $\text{MoO}_2(\text{acac})_2$, 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.

Keywords: Molybdenum reagents, molybdoenzymes, dioxobisdiethylidithiocarbamate.

Introduction

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Oxo-transfer reactions of molybdenum dioxo-bisdiethylidithiocarbamate

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 toichiometric amount of reagents there by making these methods less attractive. Additionally, there is a need for selective oxidation protocols preferable under eco-friendly conditions. Therefore, there are several attempts in this direction in developing environmentally benign oxidation strategies by employing catatic amount of reagents in the presence of molecular ixygen or hydrogen peroxide in aqueous medium. Furthermore, the oxidation of alcohols 50c by metal-oxo complexes is a well known reaction, especially by using Cr (VI) and Mn (VII) complexes. 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.

A cursory glance at the literature on molybdenum dioxo-is diethylidithiocarbamate (1) reveals that there are several attempts to conceive the reagent 1 as an oxo-transfer reagent fither in catalytic amunt or in stoichometric amounts

Apart from this, the structural and functional mimic of xo-molybdoenzymes is one of the well addressed fields of investigation.

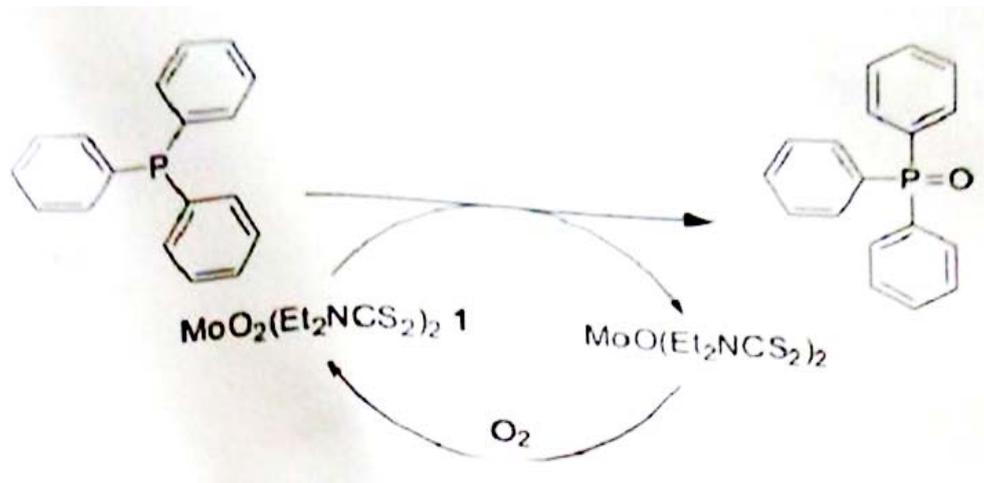
The first report on oxygen transfer reaction catalyzed by 1 as documented by Barral 66 and co-workers in 1972. In their eliminary studies, a catalytic oxidation cycle for triphenyl phosphines in presence of molecular oxygen is reported.

Later on, Holm 61 and co-workers reported the oxidations of various thiols to corresponding disulfides catalyzed by 1. Interestingly, Mitchell, 56a in 1975 has documented the first example of oxygen transfer from various organic oxides to Mo (IV) system such as

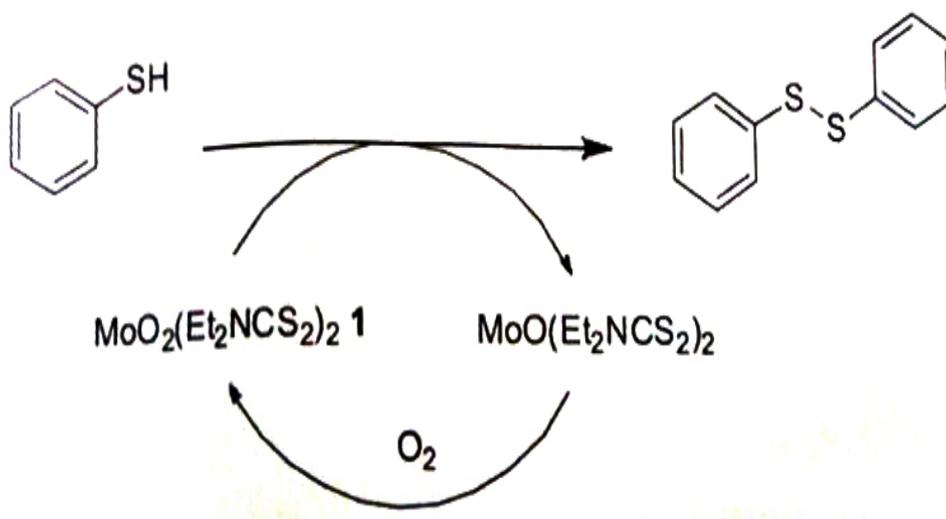
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MoO (Et₂NCS₂)₂. In this stoichiometric reaction, Mo (IV) was oxidized to Mo (VI) by sulfoxides and N-oxides to produce the corresponding sulfides and amines respectively. It is also interesting to note that sulfoxides and N-oxides are also reduced to the corresponding sulfides and amines by crude extracts containing molybdoenzymes.

Epoxidation reactions catalyzed by molybdenum (VI) eagent with alkyl hydro peroxides are well known in the literature. However in 1988 Molly 64 has reported that the epoxidation of olefin by



Oxo-transfer reaction catalyzed by molybdenum (VI) dioxo-bisdiethyldithiocarbamate.



Oxidation of thiol catalyzed by molybdenum (VI) dioxo-bisdiethyldithiocarbamate.

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 deoxygenating of epoxide by Mo (IV) analogue of 1 [MoO (Et₂NCS₂)₂] is a favorable process to produce the corresponding olefin and 1 in good yields.

Interestingly, Gomez and coworkers have reported the oxidation of olefins catalyzed by molybdenum dioxo-bisdiethyldithiocarbamate 1 in presence of aq. TBHP to produce small amount of epoxide along with the corresponding aldehyde and diol.

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