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Mo-catalyzed deoxygenation of epoxides to alkenes

Jakira Robertson, Radhey S. Srivastava *

Department of Chemistry, University of Louisiana at Lafayette, Lafayette, LA 70504, USA

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ABSTRACT

A Mo(VI)-catalyzed deoxygenation of epoxides to alkenes has been achieved using a sacrificial alcohol as a reductant. The $MoO_2(dtc)_2$ (dtc = diethyl dithiocarbamate) was proved to be a better catalyst than the other molybdenum based catalysts examined. Of the reducing agents examined, secondary alcohol, 2,4-dimethyl-3-pentanol was the most efficient and proved to be a better potential hydrogen donor. The reaction is very clean and the product yield ranges from moderate to excellent, with almost no byproduct(s) detected except, 2,4-dimethyl-3-pentanone, which is the oxidized product of 2,4-dimethyl-3-pentanol.
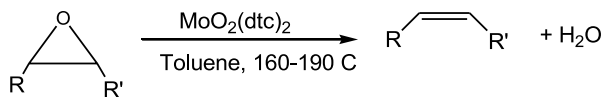
1. Introduction

The deoxygenation of epoxides to olefins is a fundamental synthetic transformation in organic [1] and biomolecular chemistry [2]. Epoxidation/deoxygenation would provide a useful protection/deprotection sequence for the multiple bonds and a number of methods have been devised to accomplish this transformation [2a,2b,3]. Though the reverse oxygenation of alkenes has been well scrutinized and extensively applied in organic synthesis [4], the metal-catalyzed deoxygenation of epoxides into alkenes is less explored. Acid catalysts, such as mineral acids [5], zeolites [6], or metal oxides [7,8] were used for dehydration. The major disadvantage of these methods is their low selectivity and low functional group tolerance as well as safety concerns. The zinc [9], ruthenium [10], or rhenium [11]-catalyzed dehydration reactions have been reported. Sharpless et al. group has developed an effective method for the deoxygenation of epoxides using stoichiometric amounts WCl_6 and ^nBuLi [12,13]. Since then a variety of catalytic systems have been developed for the deoxydehydration and deoxygenation of polyols and epoxides respectively using rhenium and ruthenium metal complexes such as $MeReO_3$, NH_4ReO_4, $ReIO_2(PPh_3)_2$, $RuCl_2(DMSO/TMSO)_4$, and $[Cp*Ru(CO)_2]_2$ in the presence of PPh_3,

H_2, or Na_2SO_3, hydroaromatics, primary, secondary, and benzylic alcohols as reductants [11,14] (Scheme 1).

Re-catalyzed stereospecific deoxygenation of inactivated aliphatic epoxides has been reported recently [15]. Other important progress in this area is the heterogeneous catalysis using Au or Ag nanoparticles as the catalyst [16] and another heterogeneous copper catalysts $[Cu(CF_3CO_2)_2$ and IMesCuCl] in the presence of diazo malonate as reductant [17]. The rhenium(VII) oxide is found more active and more selective than any of the traditional acid catalysts tried. The drawback of the application of rhenium-based catalysts could be its limited natural abundance. Mo is much cheaper and also active in oxygen atom transfer (OAT) reactions like oxidations and deoxygenations. In nature molybdenum-containing enzymes, usually bound by the pterin (pterin = 2-amino-4(1H)-pteridinone) cofactor, are known for OAT reactions, for example in DMSO reductase and sulfite oxidase [18]. The role of molybdenum based catalysts has been amply documented [19–22]. The high-valent molybdenum complexes are stronger Lewis acids and indeed show good catalytic activity. The Lewis acidity of a catalyst plays an important role in determining its activity. The Lewis acidity of a catalyst is evidently influenced by electronic properties of coordinating ligands and in turn it would be expected that the ligand to have a significant influence on catalytic activity [23]. MoO_2L_2 complexes (L = dithiocarbamate ligands, R_2dtc-(R = Et, n-Pr, i-Bu) were studied for oxygen atom transfer reactions [24]. In fact, Mo(IV), $[MoO(S_2CNEt_2)_2]$ were applied for deoxygenation of epoxides earlier [25].

* Corresponding author.
E-mail address: rss@louisiana.edu (R.S. Srivastava).
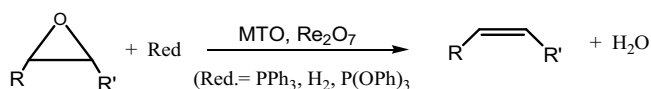
Scheme 1. Deoxygenation of epoxides with Re catalysts.

Table 1
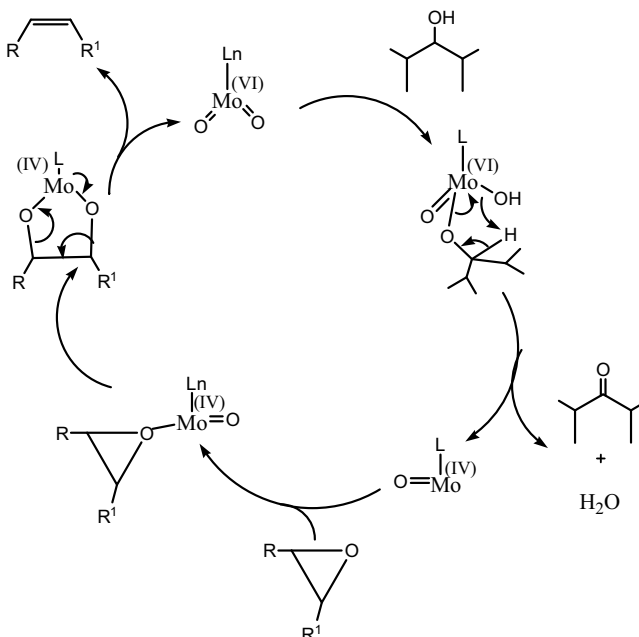Deoxygenation of styrene oxide at 160 °C for 24 h.

Entry	Catalysts	Styrene (%)
1	Molybdenum metal powder	Trace
2	Sodium molybdate	Trace
3	MoO_3	Trace
4	$MoO_2(acac)_2$	2
5	Ammonium molybdate	5
6	$Mo(CO)_6$	24 (ethyl benzene trace amount)
7	$MoO_2(dtc)_2$	75

Based on recent studies on the use of rhenium and ruthenium complexes as valuable catalysts for organic reactions [26], we initiated a project studying the deoxygenation of epoxides with inexpensive, commercially or readily available molybdenum catalysts and practical reductants. Molybdenum compounds are much cheaper than rhenium and ruthenium compounds and the Mo-compounds are mostly commercially available or can be easily made. Herein, we now report the inexpensive molybdenum catalyzed deoxygenation of epoxides to alkenes using a relatively small amount of a sacrificial alcohol as a reductant under relatively mild reaction conditions.

2. Results and discussion

Our first efforts focused on the investigation of inexpensive molybdenum-based catalysts for the deoxygenation of styrene oxide to styrene. Subsequently we concentrated on the examination of various commercially available or easily synthesized molybdenum compounds for the deoxygenation of epoxides (Table 1). Molybdenum metal (Table 1, entry 1) showed little activity in the deoxygenation of styrene oxide, as did sodium molybdate (Table 1, entry 2). Likewise, molybdenum (VI) oxide, MoO_3 (Table 1, entry 3), $MoO_2(acac)_2$ (Table 1, entry 4), and ammonium molybdate (Table 1, entry 5) showed little or no activity in deoxygenation reaction. However, Mo $(CO)_6$ (Table 1, entry 6) and $MoO_2(dtc)_2$ (Table 1, entry 7) showed relatively good activity for deoxygenation of styrene oxide. Since the MoO_2 $(dtc)_2$ was the best performing catalysts tested in our deoxygenation of styrene oxide, we decided to adapt the $MoO_2(dtc)_2$ in order to optimize the catalytic behavior of these complexes.

After optimization of catalysts, we started to study the preliminary optimization of reaction conditions for the deoxygenation of epoxide with respect to solvent, reductant, and temperature. An initial reaction was originated with styrene oxide, $MoO_2(dtc)_2$ (10 mol%) in the presence and of sacrificial alcohol (2,3-dimethyl-3-pentanol), a good amount of styrene was produced. No product were detected in the absence of 2,3-dimethyl-3-pentanol. The other alcohols such as MeOH, EtOH, ^{n}PrOH, 1-butenol, 1-octanol, Hexyl alcohol, 2-methyl-2-butanol, iso-amyl-alcohol, and 3-methyl-1-butanol, which acts as reductant as well as a solvent, gave alkenes in poor yields. Likewise reaction in diols and triols such as ethylene glycol, 1,2-propanediol, and glycerol produces large amounts of uncharacterized byproducts in GC–MS. The attempted deoxygenation of styrene oxide in water showed no conversion and not even traces of any of the expected products detected. Anhydrous and hydrated toluene, THF, and dichloroethane were also examined for deoxygenation of styrene oxide and finally we found that anhydrous toluene produces better yield than other solvents investigated.

Scheme 2. Proposed catalytic cycle for $MoO_2(dtc)_2$-catalyzed alcohol driven deoxygenation reaction. Possible reaction mechanism.

Deoxygenation of styrene oxide was carried out as a model substrate in anhydrous toluene at 160 °C in the presence of $MoO_2(dtc)_2$ (10 mol% – Mo) with 2,4-dimethyl-3-pentanol as a reductant that produced styrene in 75% yield for 24 h. The addition of 4 Å molecular sieve does not change the product yield. Next we optimized a range of temperatures and found that 160 °C is the best temperature for the model substrate for optimum yield of alkene. Temperature for the catalytic reaction involving less reactive epoxide was raised up to 190 °C, to get better yield of alkenes.

With the optimized reaction conditions in hand, a variety of epoxides varying from terminal to cyclic epoxides were subjected to the deoxygenation reaction (Table 2). The deoxygenation of all the activated epoxides (bearing a phenyl group) such as styrene oxide, ethyl-3-epoxyglacidate, 1,2-epoxy-3-phenoxypropane, and α,β-epoxy carbonyl compounds produce better deoxygenated products than inactivated linear and cyclic epoxides. Thus we found that when styrene oxide subjected to deoxygenation in the presence $MoO_2(dtc)_2$ catalyst, 2,4-dimethyl-3-pentanol as reductant in the anhydrous toluene at 160 °C produced styrene in 75% yield (Table 2, entry 1). However, the terminal epoxide, 1,2-epoxyhexane having an aliphatic group is very sluggish and produced only a trace amount alkene (Table 2, entry 2). We also examined functional group tolerance of the epoxides. Accordingly, we examined the water-sensitive ether and ester bond tolerance under these reaction conditions. Catalytic reaction of 1,2-epoxy-3-phenoxy propane, a phenolic ether, is slow and produced a low yield of alkene, 25% (Table 2, entry 3). The reaction with disubstituted epoxides (ethyl-3-phenylglycidate) occurred smoothly with 53% yields of alkene (Table 2, entry 4). The dicarbonyl epoxide such as (2R,3S)-dimethyl oxirane-2,3-dicarboxylate bearing an ester linkage was sluggish and produced the corresponding alkene in 17% for 24 h at 160 °C and 33% for 48 h at 190 °C (Table 2, entry 5). The α, β -carbonyl *(trans*-1,3-diphenyl-2,3-epoxypropan-1-one), a keto epoxide produces α, β-unsaturated ketone in excellent yields (Table 2, entry 6). Similarly the cyclic epoxides such as 1,2-epoxycyclododecane and cyclohexeneoxide are not very active and produce small amounts of the corresponding alkene in 15% and 12% respectively at 190 °C for 24 h (Table 2, entry 7 and 8). *Trans*-stilbene