Molybdenum Catalyzed Deoxydehydration of Aliphatic Glycols Under Microwave Irradiation

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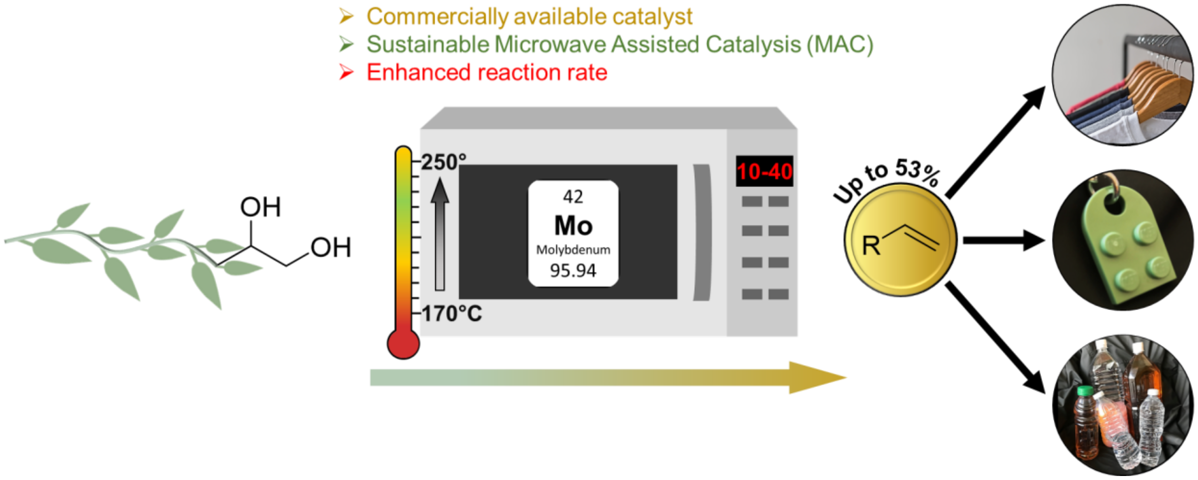
Graphical Abstract for Table of Contents



Abstract

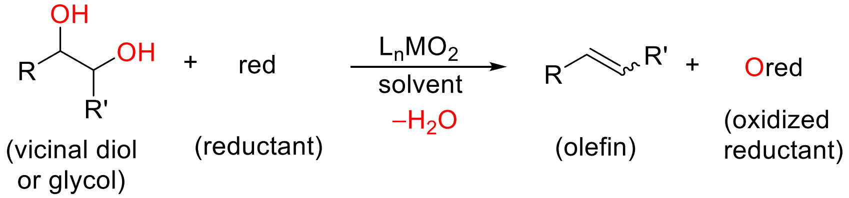
The effectiveness of microwave irradiation in promoting the deoxydehydration of aliphatic diols using dioxomolybdenum catalysts has been evaluated. The commercially available molybdenum precursor $MoO_2(acac)_2$ was found to be a superior catalyst as compared to dioxomolybdenum complexes stabilized by aminebisphenol ligands under these conditions. Octane-1,2-diol and decane-1,2-diol were converted to the corresponding olefins in 40–53% yields in 40 mins at 220–230 °C; this is a significant reduction in reaction time and higher activity when compared to reactions performed using conventional heating. More importantly, a similar yield (48%) of 1-decene could be achieved within 10 mins from a reaction carried out at 250 °C.

Key Words

Deoxydehydration, Molybdenum, Glycols, Olefins, Microwave.

Introduction

Olefins are currently produced from fossil resources through petroleum refining while the realization of a sustainable chemical enterprise demands more eco-friendly sources for such chemical feedstock [1–3]. Lignocellulosic biomass is such a resource but is saturated in oxygen functionalities such as hydroxyl groups [4]. Successful deoxygenation of biomass-derived molecules could yield useful olefins, thus reducing or even replacing the need to extract such compounds from petroleum sources [5–8]. Deoxydehydration (DODH) of glycols is a promising strategy for producing alternate platform chemicals from biobased molecules [9–13]. This one-step reaction converts glycols (vicinal diols) into corresponding olefins using an oxometal catalyst with assistance from a sacrificial reductant (Scheme 1) [14,15]. Catalytic DODH reactions based on rhenium complexes are widely explored using various reductants and are generally efficient [16–28]. Molybdenum and vanadium catalysts on the other hand are desirable as they are cost-effective, but are less efficient and require forcing reaction conditions including higher reaction temperatures and longer reaction times when compared to their rhenium counterparts [29–40].



Scheme 1. Oxometal catalyzed deoxydehydration (DODH) of glycols to olefins.

A variety of glycols have been evaluated in the DODH reaction to establish a broad substrate scope [41–51]. Although they are the more challenging substrates, aliphatic glycols more closely represent biobased glycols in reactivity compared to the aromatic/benzylic glycols [29]. Our group is interested in expanding the scope of molybdenum-catalyzed DODH reactions including the development of structure-property relationships using auxiliary ligands to support the dioxomolybdenum core $\{[MoO_2]^{2+}\}$ along with the use of practical reductants and solvents [52–54]. However, we've achieved little success in using aliphatic diols as substrates under our optimized reaction conditions. In this respect, Fristrup and group reported the DODH of hexane-1,2-diol using the commercially available ammonium heptamolybdate (AHM) as a catalyst with isopropanol as the reductant (Figure 1). The addition of a base (Bu_4NOH, 15 mol%) resulted in a maximum olefin yield of 77% (up from 46% with no base) [36]. Similarly, Vos and Stalpaert studied $MoO_2(acac)_2$ and the effects of β-diketones for *in situ* formation of the active catalyst. The bulky nature of 2,2,6,6-tetramethylheptanedione (TMHDH) was demonstrated to prevent oligomerization of the molybdenum center, thus preserving catalytic activity. Under optimized conditions (10 mol% $MoO_2(acac)_2$ and 4 eq. TMHDH with respect to substrate), hexane-1,2-diol yielded 93% olefin product as opposed to 15% using only $MoO_2(acac)_2$ [32]. Kilyanek and Tran developed an (ONO)-type bis(phenolate) molybdenum catalyst and used it in the DODH of octane-1,2-diol. They examined the effects of triphenylphosphine oxide coordinated with the molybdenum center and found increased yields of up to 59% 1-octene at 150 °C over 48 h when compared to their uncoordinated counterpart [31]. In addition, Gebbink and coworkers also used octane-1,2-diol, catalyzed by a Cp*-based dinuclear molybdenum complex, $[Cp^{*}MoO_2]_2O$. Using a 2 mol% catalyst loading, they achieved an impressive turnover number of over 30 per catalyst, yielding up to 65% 1-octene from octane-1,2-diol at 200 °C in 15 h using *m*-dichlorobenzene as solvent. $MoO_2(acac)_2$ produced 1-octene in 47% yield under similar conditions using anisole as solvent [55].

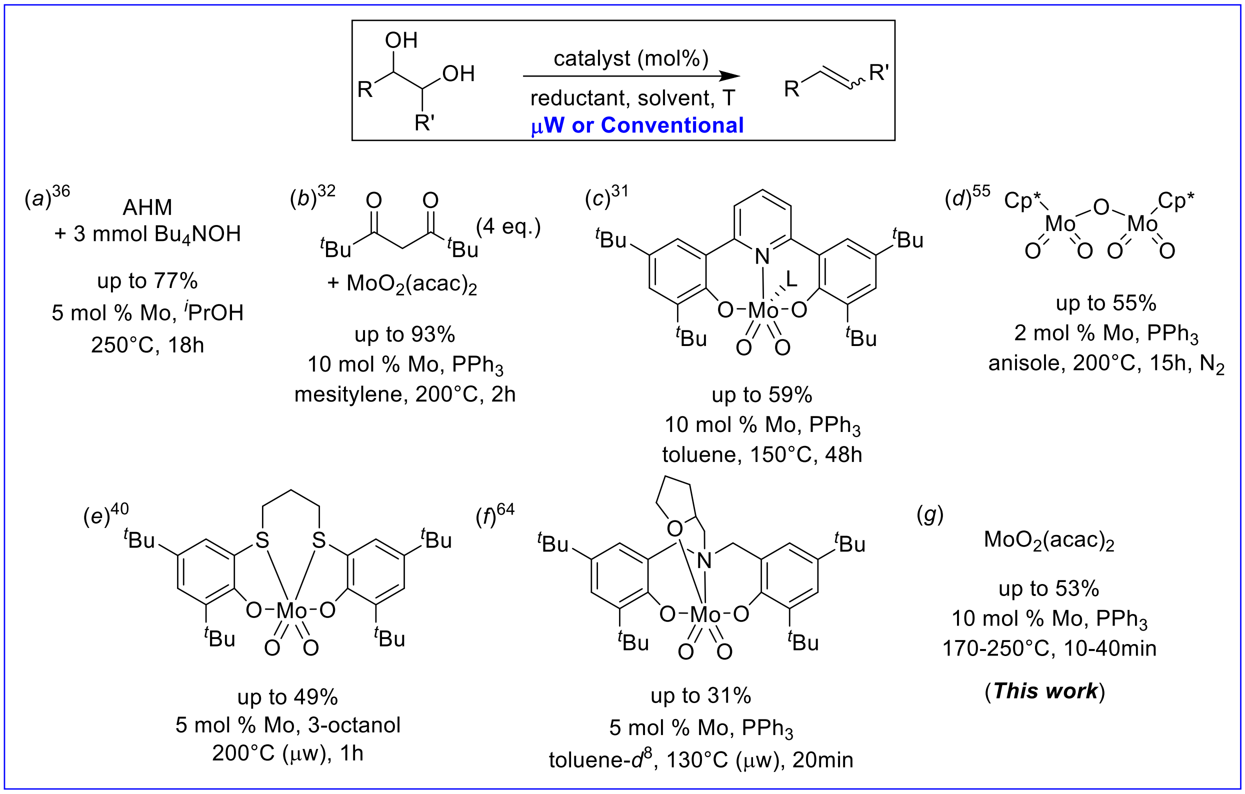
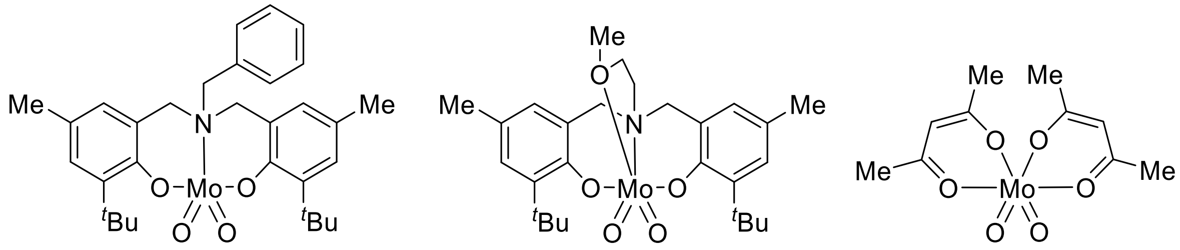


Figure 1. DODH of glycols by selected Molybdenum complexes.

The use of microwave heating has been demonstrated to increase reaction rate and yields in various synthetic processes including homogeneous and heterogenous catalysis [56–60]. It is seen as a greener method of energy transfer that may one day replace the relatively inefficient conventional heating used in the lab today [61]. So far, only a few studies of microwave-assisted DODH catalysis are known and significant reduction in reaction times have been reported. Ullah and Herrero reported formic acid catalyzed DODH yielding 56% allyl alcohol from glycerol in 10 mins at 260 °C under microwave irradiation; this was at least an order of magnitude more energy efficient when compared to runs using conventional heating [62]. Kim and coworkers demonstrated that galactaric acid can be quantitatively (97%) converted to the corresponding diene (muconate) using methyltrioxorhenium (MTO) as a catalyst and 1-heptanol as a reductant/solvent at 250 °C in 30 mins [63]. As for the use of oxomolybdenum complexes in DODH reactions, to the best of our knowledge, only two reports have explored the use of microwave heating. A dioxomolybdenum catalyst based on an aminebisphenol ligand featuring a furanyl pendant arm produced up to 31% yield of stilbene upon DODH of substituted hydrobenzoin within 20 min at 130 °C [64]. Okuda and group found that microwave irradiation facilitated DODH catalysis at lower temperatures (Figure 1). Dioxomolybdenum complexes featuring (OSSO)-type bis(phenolate) ligands effected DODH of 1,4-anhydroerythritol to dihydrofuran in 49% yield with an 89% conversion of the diol at 200 °C in 1 h as opposed to 18 h using conventional heating; the reaction could also be effected at 160 °C although with significantly lower yields [40]. Due to the limited amount of prior work in this area, we became interested in evaluating the utility of microwave irradiation in promoting DODH reactions, especially those of aliphatic diols.

Results and Discussion:



(**1**) (**2**) (**3**)

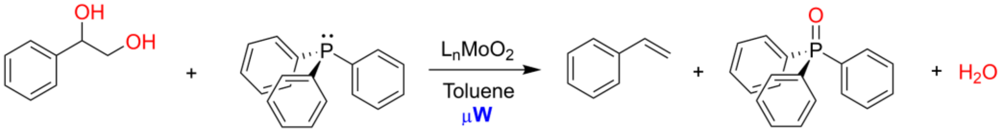
Figure 2. Catalysts selected for screening.

To assess the beneficial effect of microwave irradiation in facilitating DODH reactions, we began our investigation by studying the conversion of a prototypical substrate 1-phenyl-1,2-ethanediol (styrene glycol) to styrene using dioxomolybdenum catalysts **1** and **2** (Figure 2). These catalysts featuring aminebisphenolate ligands were previously found to be effective in promoting the DODH of styrene glycol under conventional heating [53]. Catalysts **1** and **2** produced styrene in 14% and 21% yields respectively in 40 mins under microwave irradiation {glycol (0.5 mmol),

PPh_3 (1.5 equiv.), [Mo] (10 mol%) in toluene at 170 ^{o}C} (Table 1, entries 1 and 2), which is a significantly shorter reaction time compared to that required for conventional heating (24 h). Surprisingly, a similar reaction conducted using commercially available $MoO_2(acac)_2$ (**3**) as catalyst produced a 24 % yield of styrene in 10 minutes at 68 % conversion, and the yield increased to 51% in 40 minutes at complete conversion of the diol (Table 1, entries 3-5). The molybdenum center in the oxometal catalyst, being electrophilic, is also known to promote dehydration of the vicinal diol resulting in carbonyl (C=O) compounds (aldehydes and ketones) under these conditions [36,37]. Carbonyl compounds can also result from an oxidative cleavage of the diol *via* a glycolate intermediate; this results in a reduction of the metal center [31,65,66]. The extent of oxidative cleavage and/or dehydration (C=O products) observed under our reaction conditions was relatively minimal (≤5%). Although a complete conversion of the diol was observed at 40 mins, we were unable to detect any other organic products besides the olefin and C=O products. The low mass balance observed in these reactions could be attributed to either thermal degradation of the diol substrate at the high reaction temperatures or the formation of acetal or ketal products which could not be detected and accounted for [55].

Consequently, dioxomolybdenum complexes supported by ancillary ligands were excluded for subsequent studies, and the readily available catalyst precursor $MoO_2(acac)_2$ was selected for further optimization. A solvent screen was conducted next to gauge dependence of styrene yield on solvent polarity (Table 2). Aromatic solvents such as toluene, mesitylene, and chlorobenzene worked best for the DODH of styrene glycol producing styrene in 23−51% yield (Table 2, entries 1-3). Polar solvents such as *N*,*N'*-dimethylpropyleneurea (DMPU) and 2-propanol were found to hinder catalytic activity as evidenced by low conversions (Table 2, entries 4-5) although a high selectivity (78%) for the olefin product was noted in DMPU. This suggests that DMPU can suppress competing reactions that are occurring under these conditions. Since DMPU is a coordinating solvent, it can potentially interact with the metal center to reduce its electrophilicity and thus suppress competing reactions [67,68]. Our overall observations regarding solvent effects are consistent with those from prior studies where aromatic solvents were found to be superior at catalyzing DODH reactions [31,53,55].

Table 1. Catalyst screening for DODH of styrene glycol under microwave irradiation.[a]



entry	catalyst	T (°C)	time[b] (min)	yield[c] (%)		conversion	selectivity
				C=C	C=O	(%)	(%)
1.	**1**	170	40	14	4	67	20
2.	**2**	170	40	21	5	90	23
3.	**3**	170	10	24	2	68	36
4.			20	31	4	84	37
5.			**40**	**51**	**4**	**>99**	**51**

[a] Reaction conditions: styrene glycol (0.5 mmol), PPh_3 (0.75 mmol, 1.5 equiv.), and Mo catalyst (0.05 mmol, 10 mol%) in toluene (ca. 2.5 mL) in a Biotage® vial under microwave irradiation. [b] Time recorded after reaction mixture hits 170 °C, ~3 min. [c] Yields were determined using 1,3,5-trimethoxybenzene as an internal standard *via* ^{1}H NMR spectroscopy. “C=C” refers to the olefin product while “C=O” refers to aldehydes formed because of oxidative cleavage and dehydration reactions. Selectivity both refer to the olefin product.

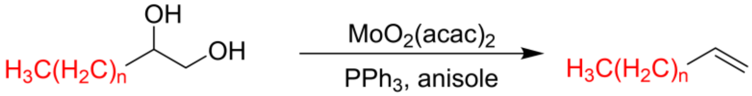
Table 2. Solvent screen for microwave-assisted DODH of styrene glycol.[a]

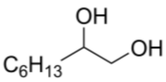
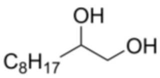
entry	solvent	yield[b] (%)	conv. (%)	select. (%)
1.	**Toluene**	**51**	**>99**	**51**
2.	Mesitylene	23	73	31
3.	**Chlorobenzene**	**48**	**>99**	**48**
4.	DMPU	5	6	78
5.	Isopropanol	4	8	47

[a]Reaction conditions: styrene glycol (0.5 mmol), PPh_3 (0.75 mmol, 1.5 equiv.), and Mo catalyst (0.05 mmol, 10 mol%) in solvent (ca. 2.5 mL) in a Biotage® vial under microwave irradiation. Reactions were run for 40 mins, and time was recorded after reaction mixture hits 170 °C, ~3 min. [b]Yields were determined using 1,3,5-trimethoxybenzene as an internal standard *via* ^1H NMR spectroscopy. Yield and selectivity both refer to the olefin product.

Toluene was initially chosen for further optimization of DODH of an aliphatic diol (octane-1,2-diol) based on the solvent screen. However, no olefin product was detected in a catalytic reaction performed at 170 °C {octane-1,2-diol (0.5 mmol), PPh_3 (1.5 equiv.), [Mo] (10 mol%) in toluene}, albeit conversion of diol was observed both under conventional (16%) and microwave heating (68%) (Table 3, entry 1). The significantly higher conversion observed using microwave heating implies that thermal degradation of the diol is prominent under these conditions and could account for some of the observed mass imbalance. We pivoted to running these catalytic reactions on aliphatic diols in anisole as a solvent based on a recent work by Gebbink *et al.* which documented that acceptable yields (47%) of 1-octene could be achieved with $MoO_2(acac)_2$ over 15 hours using anisole at 200 °C [55]. When the DODH reaction of octane-1,2-diol was attempted using conventional heating (195 °C) for 21h in anisole, a 38% yield of 1-octene was obtained at complete conversion of the diol (Table 3, entry 2). A similar reaction (Table 3, entry 2) performed for 40 mins under microwave irradiation produced a 7% yield of 1-octene at 32% conversion of the diol (21% selectivity). The lower yield using conventional heating (38%) compared to the literature precedence (47%) could be attributed to a difference in reaction conditions as we did not use a N_2 atmosphere for our catalytic reaction. This hypothesis is supported by similar observations made by Gebbink and coworkers who recorded a drop (~17%) in 1-octene yield when their reaction was carried out under aerobic conditions using $[Cp^*MoO_2]_2O$ [55].

Table 3. DODH of aliphatic diols using $MoO_2(acac)_2$.[a]

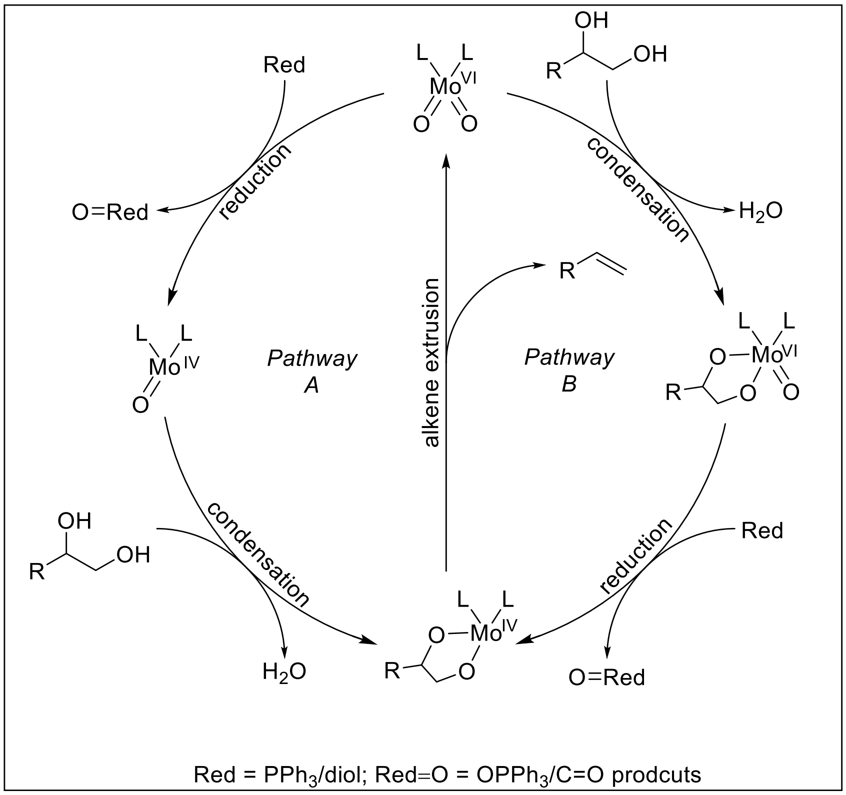


entry	substrate	T (°C)	time[b]	yield[c] (%)		conversion	selectivity
			(min)	C=C	C=O	(%)	(%)
1.[d]		170	40 (21h)	0 (0)	1 (2)	68 (16)	0 (0)
2.		195	40 (21h)	7 (38)	2 (<1)	32 (>99)	21 (38)
3.		210	40	23	2	68	34
4.		**220**	**40**	**40 (<1)**	**3 (6)**	**>99 (16)**	**40 (0)**
5.		220	40	46 (1)	2 (5)	>99 (38)	46 (4)
6.		**230**	**40**	**53**	**1**	>99	**53**
7.		250	40	51	3	>99	51
8.		**250**	**10**	**48**	**4**	>99	**48**

[a]Reaction conditions: aliphatic diol (0.5 mmol), PPh_3 (0.75 mmol, 1.5 equiv.), and $MoO_2(acac)_2$ (0.05 mmol, 10 mol%) in anisole (ca. 2.5 mL) in a Biotage® vial under microwave irradiation or if indicated in parentheses, were under conventional heating either in an oil bath (<200 °C) or an aluminum heating block (>200°C) at a stirring rate of ~600 rpm. [b]In microwave, time recorded after reaction mixture hits T (°C), ~3 mins; for reactions under conventional heating, time was recorded after 10 mins. [c]Yields were determined using 1,3,5-trimethoxybenzene as an internal standard via ^1H NMR spectroscopy. "C=C" refers to the olefin product while "C=O" refers to aldehydes formed because of oxidative cleavage and dehydration reactions. Selectivity both refer to the olefin product. [d]Reactions were run in toluene (*ca*. 2.5 mL) as solvent.

Since microwave heating is known for its ability to increase reaction rate in shorter periods of time, we opted to increase reaction temperature instead of extending the reaction time. The yield of the alkene product under microwave irradiation was found to increase at higher temperatures. The alkene product (1-octene) was obtained in 23% yield (34% selectivity) when the reaction was conducted at 210 °C for 40 mins and in a 40% yield (>99% conversion of diol) at 220 °C (Table 3, entries 3-4). The extent of oxidative cleavage of the diol (determined by ^{1}H NMR spectroscopy) under these conditions was minimal (≤3%). In contrast, a catalytic reaction performed using conventional heating at 220 °C for 40 mins generated almost no alkene product (<1%) and a relatively higher amount of oxidative cleavage was observed (6%). The same optimal conditions were next applied to DODH of decane-1,2-diol which is found to produce slightly higher yields relative to the shorter aliphatic diols. In our case, it held true with a 46% yield (Figure S1) of 1-decene at 220 °C (>99% conversion) while a reaction conducted using conventional heating over 40 mins produced negligible amount (<1%) of the alkene product along with 38% conversion of the diol (Table 3, entry 5). The yield of 1-decene increased marginally when the reaction temperature was increased to 230 °C (53%) while a slight drop was recorded beyond (250 °C; 51%) (Table 3, entries 6-7). Quite significantly, 1-decene can be obtained in a 48% yield within 10 mins at 250 °C under microwave irradiation. This represents a significant reduction in reaction time, and the use of commercially available $MoO_2(acac)_2$ as catalyst is a huge bonus from a practical standpoint. We also attempted to reuse the catalyst by adding an additional equivalent of the diol. This was performed by subjecting decane-1,2-diol to DODH catalysis at 230 °C for 20 mins (100% conversion, 41% yield, 1st run) and then cooling the reaction to room temperature before a second equivalent of diol was added to it. The reaction mixture was then heated in the microwave for further 20 mins which generated an additional 37% of the alkene product indicating that the catalyst does not lose activity and can be reused. The use of anisole as a solvent in organic transformations is attractive considering the potential for deriving it from the cleavage of lignocellulosic biomass which would make it as a green solvent [69–71].

The general mechanism for oxometal-catalyzed deoxydehydration is proposed to follow two accepted pathways (Scheme 2). Both pathways involve condensation, reduction, and alkene extrusion steps, however the order of the condensation and reduction steps are reversed between them. Pathway A involves an initial reduction of L_nMoO_2(VI), producing L_nMoO(IV). This Mo(IV) intermediate then undergoes condensation with the vicinal diol to produce L_nMo•diolate(IV), the active species for alkene extrusion; reforming L_nMoO_2(VI). Pathway B on the contrary proceeds with condensation first, forming L_nMoO•diolate(VI) which is then reduced by the reductant to yield L_nMo•diolate(IV). This common active species forms the desired alkene through alkene extrusion and restarts the catalytic cycle. Computational investigation of DODH reactions catalyzed by dioxomolybdenum centers as well as mechanistic studies based on oxorhenium catalyzed reactions suggest that the reduction of oxometal species or alkene extrusion can possibly be the rate-limiting step [21,66].



Scheme 2. Plausible mechanistic pathways of Molybdenum driven DODH.

As mentioned earlier, we did not detect any alkene product when the catalytic reaction of octane-1,2-diol was carried out at 170 °C while C=O products were generated in small amounts. The catalytic run also showed a characteristic color change from an initial pale-yellow to reddish-brown observed during these DODH reactions. This implies that the condensation of the diol with L_nMoO_2(VI) to form the glycolate intermediate and a subsequent oxidative cleavage that results in the reduction of the Mo(VI) center are feasible at 170 °C (Table 3, entry 1). Since PPh_3 is a strong reducing agent, the diol competes with PPh_3 to reduce the molybdenum center. To verify this hypothesis, we performed a time-dependent study of the DODH reaction of decane-1,2-diol at 230 °C (Figure 3) [72,73]. This study revealed that the diol is consumed at a much higher rate than the rate of formation of product supporting the argument that the diol is being used as a reductant also (*via* the metal-glycolate intermediate) in addition to possible thermal degradation. The involvement of diol substrate as a reductant was further validated using GC-MS analysis (Scheme 3 and Figures S2–S10) which detected the presence of nonanal in the reaction mixture (formed due to oxidative cleavage of the diol). In addition to nonanal, decanal and 2-decanone were also detected during GC-MS analysis. These carbonyl compounds result from dehydration of decane-1,2-diol (Scheme 3) and provide further evidence in support of the significantly higher rate of consumption of the diol and the mass imbalance observed in these catalytic reactions. The alkene extrusion step on the other hand requires a higher temperature as the olefin product is only observed at 195 °C suggesting that alkene extrusion step has a high activation barrier for this catalytic system (Table 3, entry 2) [25]. Cumulatively, the results from our studies do not conclusively favor either pathway (Scheme 2) but the significantly higher rate at which the diol is consumed could be indicative of a preference for a modified pathway A which involves condensation followed by reduction (both facilitated by the diol)to yield the $L_nMo(IV)$ intermediate. Detailed studies focusing on mechanistic investigations are currently underway in our group to delineate the competing reduction pathways and further improve these microwave-assisted DODH reactions.

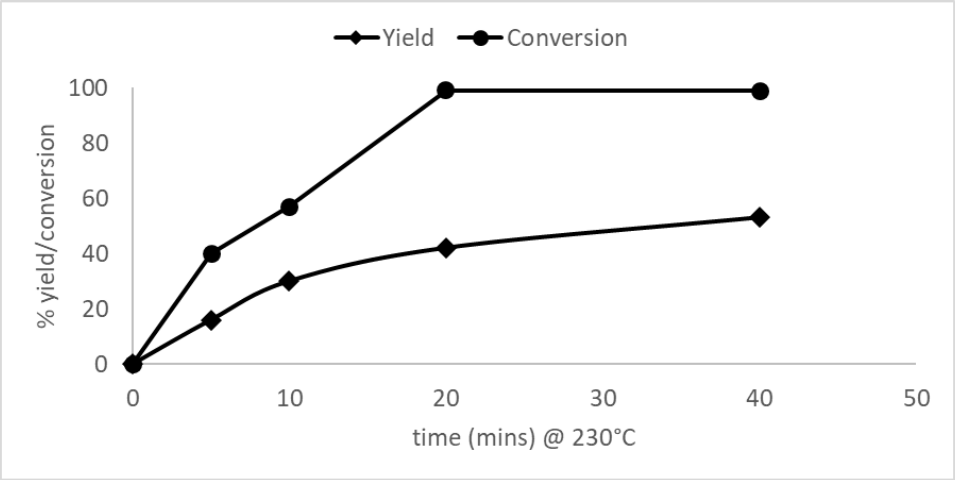
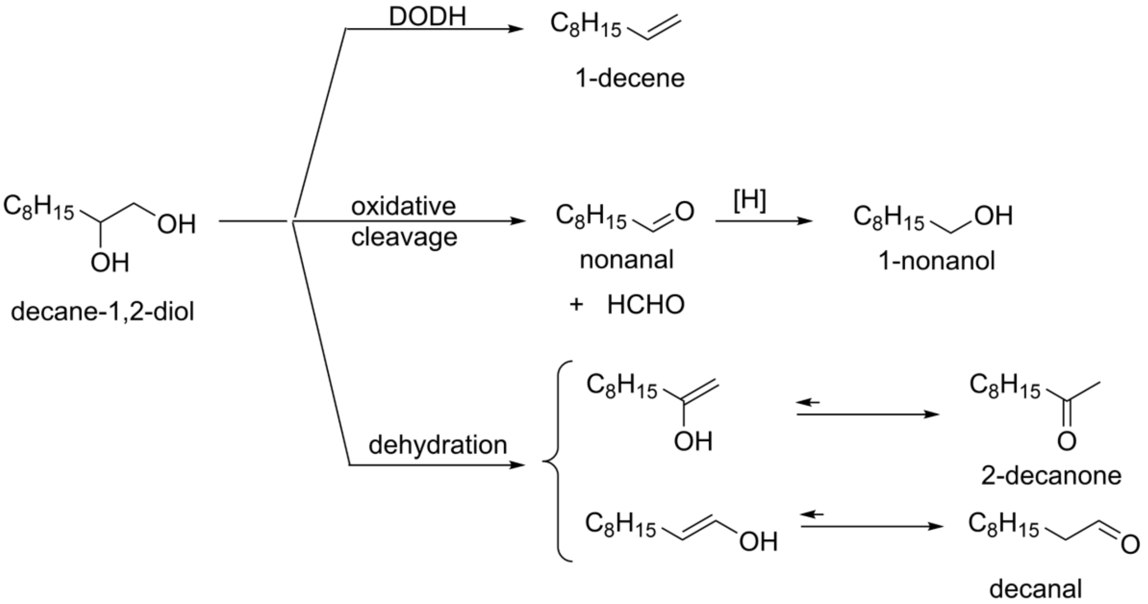


Figure 3. Plot of yield/conversion *vs* time for DODH of decane-1,2-diol at 230 °C.



Scheme 3. Compounds detected by GC-MS analysis of the DODH reaction of decane-1,2-diol.

Conclusion

In summary, microwave irradiation was found to enhance the rate of molybdenum-catalyzed DODH reaction of aliphatic diols. Commercially available $MoO_2(acac)_2$ was found to be more effective as compared to dioxomolybdenum complexes supported by aminebisphenol ligands. Under optimized reaction conditions, 1-phenyl-1,2-ethanediol was converted to styrene in 51% yield in 40 mins at 170 °C. Aliphatic diols such as octane-1,2-diol and decane-1,2-diol could be converted to corresponding alkenes in up to 53% yield in 40 mins using anisole as a solvent at 200-250 °C. GC-MS analysis of the reaction mixture provides explanation for the observed mass imbalance including the involvement of the diol substrate as a co-reductant as well as competing side reactions such as dehydration. The use of microwave heating resulted in efficient heat transfer which aided in an increased olefin yield when compared to reaction carried out using conventional heating.

Acknowledgments

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Experimental Section

General Procedures: $MoO_2(acac)_2$ catalyst was acquired from Alfa Aesar with 99% purity. Unless stated otherwise, reagents and solvents were obtained from Sigma-Aldrich and Acros (now Thermo Scientific) with ≥97% purity and were used as purchased. The diols, triphenylphosphine, and $MoO_2(acac)_2$ were stored in a desiccator. Complexes **1** and **2** were synthesized using previously reported procedures [53]. Toluene was ACS grade and anisole was of 99% purity. All ^{1}H NMR spectra were collected on a Varian 400-MR spectrometer and calibrated to the residual protonated solvent at δ 7.27 for deuterated chloroform ($CDCl_3$). The included spectra are of protons that were visible, and the bolded peaks were used to determine NMR yield. GC-MS data was collected on an Agilent 6850 series GC system connected to an Agilent 5973 using an Agilent technologies HP-5MS column (30m × 0.25mm × 0.25μm). The temperature program used was: hold at 50 ^{o}C for 2min followed by a ramp at 20 ^{o}C/min to 270 ^{o}C and hold at 270 ^{o}C for 10 mins. TGA data was collected on a TA instruments TGA Q50.

1,3,5-trimethoxybenzene (TMB): δ **6.1** (s, 3H), 3.85 (s, 9H)

Styrene: δ 5.34 (d, 1H), **5.85** (d, 1H); 6.82 (m, 1H)

Aldehyde: δ 9.5-10.0 (s, 1H)

1-octene: δ 4.98 (d, 1H), 5.05 (d, 1H), **5.87** (m, 1H).

1-decene: δ 4.96 (d, 1H), 5.02 (d, 1H), **5.85** (m, 1H)

Representative procedure for deoxydehydration reactions.

Unless otherwise stated, the following is the general procedure used to run microwave and conventional reactions.

Microwave reactions were done in a Biotage® Initiator+, Fourth Generation Microwave Synthesizer (400 W; 2.45 GHz) using their 2.0-5.0 mL vials with the included septum and stir bar. Unless otherwise stated, all reaction parameters were consistent with the following: FHT/**on**, Cooling/**on**, Pressure/**off**, Power/**off**, Stir Rate/**600 rpm**, Pre-Stirring/**30sec**, Vial Type/**2.0-5.0mL**, Initial Power/**off**, Absorption/**normal**; exceptions: toluene, mesitylene, chlorobenzene, and DMPU/**low**, isopropanol/**high**.

Microwave heating - In a pressure microwave vial, the diol substrate (0.5 mmol) was added along with PPh_3 (0.75 mmol, 1.5 equiv.) and $MoO_2(acac)_2$ (.05 mmol, 10 mol% on the basis of Mo), before placing a PTFE coated stir bar in to mix and dissolve the reagents in solvent (*ca*. 2.5 mL). The vial was capped with a septum. The reaction vial was then placed under microwave irradiation with rapid stirring. After the desired reaction time was reached, the solution was allowed to cool to room temperature before 1,3,5-trimethoxybenzene (0.010 g, .059 mmol) was added as an internal standard. Yield was determined by filtering an aliquot through a cotton plug and dissolving a few drops in $CDCl_3$ before analyzing via ^1H NMR spectroscopy.

Conventional heating - A pressure tube was charged with the same reagents and their respected quantities. A PTFE stir bar was added to dissolve the reagents in solvent. The pressure tube was then sealed with a PTFE screw cap equipped with a rubber O-ring. The tube was then placed in a preheated oil bath (< 200 °C) or an aluminum heating block (> 200 °C), depending on temperature, with rapid stirring (~600 rpm). Yield was determined in a similar manner.

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[72] The thermal stability of $MoO_2(acac)_2$ at temperatures like our catalytic conditions was evaluated using thermogravimetric (TGA) analysis (under air) which revealed that $MoO_2(acac)_2$ is stable until 170 °C beyond which a 40 % mass loss was observed till 210 °C (Figure S11). However, these results may not relate directly to our catalytic conditions due to effect of solvent, and identity of molybdenum species.

[73] A concern was raised during the peer-review process regarding the amount of time it takes for the reaction vessel to reach the applied temperature. A plot showing the change in reaction temperature as a function of time is provided as Figure S12 (the reaction under conventional heating was only monitored till 150 °C which is close to boiling point of anisole) As can be seen from the plot, both microwave and conventional heating require less than 5 minutes to reach the applied temperature.