

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

A Selective, Efficient and Environmentally Friendly Method for the Oxidative Cleavage of Glycols†

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⁵ Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

A catalytic methodology for the oxidative cleavage of vicinal diols is described as an advantageous alternative in terms of environmental impact to classical methods involving toxic oxidants. The novel strategy is based on the use of dioxomolybdenum(VI) complexes as catalysts and dimethyl sulfoxide (DMSO) as oxidant and displays high selectivity and broad scope for the glycol cleavage. In addition, the developed system is also useful for the oxidation of acyloins to diketones.

The glycol cleavage is a fundamental reaction widely used in organic synthesis, including the preparation of natural products.¹ The two major reagents for cleaving vicinal diols are periodic acid, or its salts (Malaprade reaction),² and lead tetraacetate (Criegee glycol cleavage).³ However, their use suffers from severe drawbacks, mainly their toxicity and the production of large amount of waste. In addition, sodium periodate is not effective in nonpolar solvents due to its insolubility, and it is also able to oxidize other functional groups such as alcohols, alkenes, aromatics, sulphides,.. whereas its reactions with ditertiary glycols do not proceed.⁴ Several other oxidizing systems have been developed such as BiPh₃/NBS/K₂CO₃,⁵ CrO₃,⁶ NIS,⁷ Ta(NO₃)₃,⁸ CAN,⁹... and, also hypervalent iodine compounds have been re-introduced in last years as a useful alternative.¹⁰ Nevertheless, all of them present important disadvantages from an environmentally point of view. Looking for new and cleaner reagents for this transformation, some particular catalytic systems have been reported using oxygen as a clean oxidant, although important problems such as the formation of overoxidation products, or the need for high pressures remain to be solved.¹¹

On the other hand, DMSO, which is a byproduct of the wood industry, is an inexpensive solvent with low relative toxicity that is widely used in organic synthesis and the pharmaceutical industry.¹² It is miscible with most of the common organic solvents and completely miscible with water, being present in some industrial wastewaters. Moreover, DMSO has been claimed as a green solvent suitable for replacing toxic solvents due to its high boiling point (189 °C at 760 mmHg), a very low vapour pressure (0.6 mmHg at 25 °C), and readily biodegradability.¹³ It has been also classified as a nontoxic solvent with no risk for human health by U.S. Environmental Protection Agency (EPA).¹⁴ According to the U.S. FDA solvent classification, DMSO belongs

to class 3 “solvents with low toxic potential”, and so, no health-based exposure limit is needed.

⁵⁰ In addition, besides as an organic solvent, DMSO can also act as oxidant under mild reaction conditions (Swern oxidation and its variants),¹⁵ oxygen source (Kornblum oxidation),¹⁶ thiomethyl / methylthiomethyl source,¹⁷ and one-carbon source.¹⁸

⁵⁵ Taking all this in account, herein we report a novel, selective, efficient and environmentally friendly protocol for the oxidative cleavage of 1,2-diols using the combination dioxomolybdenum(VI) complex as catalyst and dimethyl sulfoxide as oxidant.

⁶⁰ In recent years, we have been interested in the development of cleaner synthetic methodologies involving redox processes by using environmentally friendly and easily available high-valence dioxomolybdenum(VI) complexes.¹⁹ Looking for greener oxygen-acceptors in this chemistry, we have recently reported that pinacol (2,3-dimethyl-2,3-butanediol) can be used as stoichiometric reagent for the reduction of sulfoxides and nitroaromatics.²⁰ Based in that experience and the related deoxygenation of sulfoxides with glycerol,²¹ we selected easily and conveniently prepared MoO₂Cl₂(dmsO)₂ as catalyst,²² for exploring the oxidative cleavage of benzopinacol (1,1,2,2-tetraphenylethane-1,2-diol) with DMSO (Table 1).²³ After some experimentation we found that under microwave irradiation and using toluene as solvent at 130 °C only one equiv. of DMSO was needed for complete cleavage of the model diol (entries 1–2). In addition, when 0.5 equiv. of DMSO were used, a *ca.* 50% ⁷⁵ conversion was observed showing that one equiv. of the oxidant is required for complete cleavage (entry 3). Interestingly, additional solvent is not needed and so, carrying out the reaction in neat DMSO (*ca.* 0.4 mL/mmol, ~6 equiv.) also gave a satisfactory result (entry 4). Although complete conversion was ⁸⁰ observed when the amount of DMSO was reduced to 2 equiv., minor amounts of diphenylmethanol, as a disproportion-derived byproduct, were generated, probably due to incomplete solubilisation of the substrate (entry 5). So, an excess of DMSO was used for better homogeneity of the reaction mixture and to ⁸⁵ avoid the formation of side-products. Moreover, under the optimized conditions of entry 4, other dioxomolybdenum(VI) complexes such as MoO₂Cl₂(dmf)₂, MoO₂Cl₂(OPPh₃)₂, MoO₂(acac)₂, and MoO₂Cl₂(bipy) afforded similar results.²⁴ The reaction can also be conducted at lower temperatures although ⁹⁰ slightly longer reaction times were needed below 100 °C (entries

6–7). Moreover, using ~1 g of the substrate, the catalyst loading could be reduced to 0.1 mol% without affecting the reaction time or the isolated yield (entry 8). Control experiments without catalyst showed that DMSO alone, which has not been previously described as reagent for the oxidative cleavage of diols, provides a full conversion for this highly activated diol, although significant amounts of diphenylmethanol and bis(diphenylmethyl)ether were also generated (entries 9–10).²⁵ Finally, we showed that under conventional heating the reaction also proceeds leading to complete conversion after 1.5 h at 100 °C (entry 11).

Table 1 Optimization of the reaction conditions for the Mo-catalyzed oxidative cleavage of benzopinacol with DMSO.

Entry	Solvent	DMSO (equiv.)	[Mo] (mol%)	Temp. (°C)	Time (min)	Yield ^a (%)
1	toluene ^b	4	2	110	5	(76)
2	toluene ^b	1	2	130	10	90 (100)
3	toluene ^b	0.5	2	130	10	(55)
4	–	6	2	130	10	94 (100)
5	–	2	2	130	10	(100) ^c
6 ^d	–	6	2	110	10	(>97)
7 ^d	–	6	2	90	20	(>97)
8 ^e	–	5	0.1	130	10	93 (100)
9 ^d	–	6	–	130	10	54 (100) ^f
10 ^d	–	6	–	160	10	61 (100) ^f
11 ^g	–	6	2	100	90	92 (100)

^a Based on the starting diol; in brackets conversion estimated by ¹H NMR (300 MHz) from the crude reaction mixture. Reactions were conducted with 0.5 or 1 mmol of benzopinacol under microwave irradiation (maximum wattage 300 W, see ESI† for details), unless otherwise stated. ^b 1 mL of solvent was used. ^c ~10% of diphenylmethanol was formed as byproduct. ^d Reactions performed in DMSO-d₆. ^e Carried out with 3 mmol of diol. ^f Diphenylmethanol and bis(diphenylmethyl) ether were also formed as byproducts. ^g Reaction conducted under conventional heating.

Table 2 Oxidative cleavage of 1,2-diols with DMSO catalyzed by MoO₂Cl₂(dmsO)₂

Entry	1,2-Diol ^a	T (°C)	t (min)	Product(s)	Yield (%) ^b
1		130	10	Ar ¹ = Ar ² = 4-MeC ₆ H ₄	86
2		130	10	Ar ¹ = Ph; Ar ² = 4-BrC ₆ H ₄	87
3		130	10	Ar ¹ = Ar ² = 4-ClC ₆ H ₄	89
4		130	10		91
5 ^c		130	10		93
6 ^{d,f}		130	10		<5
7 ^e		100	60		91
8		130	10	Ar = 4-MeC ₆ H ₄	93
9		130	10	Ar = 4-MeOC ₆ H ₄	87
10		130	10	Ar = 4-BrC ₆ H ₄	84
11		130	10	Ar = 4-ClC ₆ H ₄	89
12		130	10	Ar = 3,5-F ₂ C ₆ H ₃	91
13 ^f		150	20		93 ^g
14 ^{f,h}		130	40		95 ^g
15		130	10		93
16 ^f		130	20		82
17 ^{f,h}		100	15		63 ⁱ (87) ^g
18 ^h		130	10		94
19 ^{c,h}		130	10		93
20 ^d		130	10		0
21 ^{e,h}		120	120		89
22		130	10	Ar = 4-MeOC ₆ H ₄	92
23		130	10	Ar = 4-ClC ₆ H ₄	95
24		130	20	Ar = 2-ClC ₆ H ₄	83
25		130	10	Ar = 4-BrC ₆ H ₄	91
26 ^{f,h}		170	10		95 ^g
27 ^{f,h}		180	5		80 ^{g,j}

^a Starting diols bearing two stereogenic centers were used as variable mixtures of diastereoisomers. ^b Yield of crude carbonyl compound (purity > 90% by ¹H NMR). ^c Reaction conducted with 0.2 mol% of the catalyst and 2 equiv. of DMSO starting from 3 mmol of glycol. ^d Reactions conducted without catalyst. ^e Reaction conducted under conventional heating. ^f Reactions performed in DMSO-d₆. ^g NMR yield using dibromomethane or 1,3,5-trimethoxybenzene as internal standard. ^h Reactions conducted in the presence of activated 4 Å molecular sieves. ⁱ

15 With these optimized conditions, we embarked on the evaluation of the substrate scope (Table 2). We first evaluated a series of ditertiary glycols which, interestingly, cannot be cleaved using periodates (entries 1–14). Gratifyingly, glycols bearing aromatic rings with either electron-donating or electron-withdrawing groups could be cleaved using our developed methodology, leading in all cases to high yields of the corresponding ketones (entries 1–3). Likewise, 2,3-diphenylbutane-2,3-diol was efficiently oxidized to acetophenone even when the catalyst loading was lowered to 0.2 mol% (entries 4 and 5), while no reaction was observed for this substrate in the absence of catalyst when the reaction was performed at 130 °C (entry 6). Moreover, the reaction also proceeds under conventional heating, leading to full conversion after 1 h at 100 °C (entry 7). Analogous substrates having substituents of different electronic nature in the aromatic rings are also efficiently cleaved under the optimized conditions (entries 8–12). Furthermore, ditertiary glycols bearing only aliphatic groups also afforded the corresponding ketones in good yields, although higher temperatures and/or longer reaction times were required (entries 13 and 14).

Isolated yield after column chromatography. Obtained as ca. 1.5:1 mixture of diastereoisomers. ^j An unidentified side-product was also formed.

Next, we examined the oxidative cleavage of diols having both a tertiary and a secondary alcohol (entries 15–17). Noteworthy, these substrates provided the corresponding ketones/aldehydes in good yields, as well.

Interestingly, disecundary glycols are also efficiently cleaved under the optimized conditions, though the presence of activated 4 Å molecular sieves resulted to be necessary for improving the selectivity of the process. For the oxidative cleavage of 1,2-diphenylethane-1,2-diol we also confirmed that the catalyst loading could be lowered to 0.2 mol% (entries 18 and 19), and no reaction was observed in the absence of catalyst (entry 20). Moreover, full conversion and good yield of benzaldehyde were obtained under conventional heating for 2 h at 120 °C (entry 21). Other 1,2-diarylethane-1,2-diols with either electron-donating or electron-withdrawing groups are also cleaved in good yields under the optimized conditions (entries 22–25).

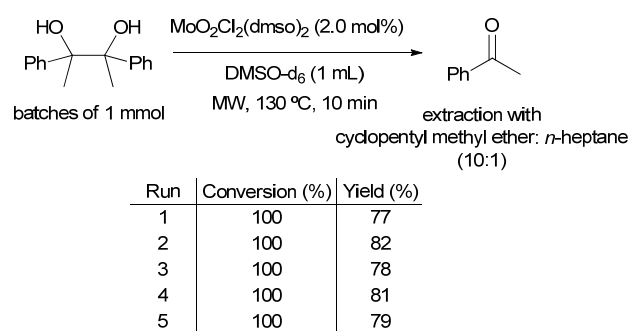
Finally, a tertiary-primary glycol (entry 26) and even a secondary-primary glycol (entry 27) could also be converted into the corresponding carbonyl compounds in good yields, although higher temperatures were required for these substrates.²⁶

Notably, overoxidation to the corresponding carboxylic acids was never observed for secondary glycols and all the reported cleavages exclusively yield the corresponding aldehydes and/or ketones.

In addition, the obtained carbonyl compounds could be easily isolated in high purity by simple extraction to remove the Mo catalyst, without the need of further purification by column chromatography. In a representative experiment, a mixture of 2,3-diphenylbutane-2,3-diol (242 mg, 1 mmol) and MoO₂Cl₂(dmsO)₂ (7 mg, 2.0 mol%) in DMSO (0.4 mL, ~6 mmol) was irradiated in a sealed tube in the microwave cavity at 130 °C for 10 min. Then, the reaction mixture was cooled to room temperature and an ethereal solvent (Et₂O or cyclopentyl methyl ether, 5 mL) and H₂O (5 mL) were added. The layers were separated and the aqueous layer extracted with the ether (2 × 5 mL). The combined organic layers were washed with water to completely remove the excess of DMSO, dried over anhydrous Na₂SO₄, filtered, and the volatiles (solvents and the remaining dimethyl sulphide generated as byproduct) were removed under reduced pressure to yield acetophenone in pure form (218 mg, 91% yield).

The stability and reusability of a catalyst are crucial factors in the sustainability of a catalytic procedure and the development of potential practical applications. Thus, to assess the recyclability of the dioxomolybdenum complex in the reported process, we performed the oxidative cleavage of 2,3-diphenylbutane-2,3-diol under the developed conditions (microwave irradiation, 130 °C, 10 min) using DMSO-d₆ in order to determine the conversion of the reaction by ¹H-NMR. The acetophenone produced in the first run could be in-flask extracted from the reaction mixture using minimal amount of a 10:1 mixture of cyclopentyl methyl ether and *n*-heptane (2 × 1 mL). The following batches of glycol, dissolved in DMSO-d₆ (0.2 mL), were added to the DMSO-phase containing the catalyst, and the reactions conducted under the same reaction conditions revealing similar catalyst activity. Remarkably, we were able to reuse the catalytic system for at

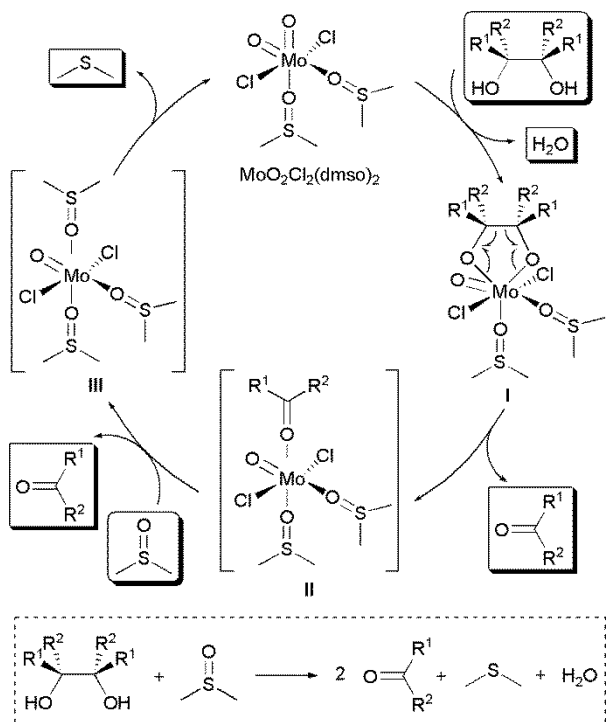
least five times with a negligible change in its activity (Scheme 1).



Scheme 1 Recycling study of the Mo-catalyzed oxidative cleavage of 2,3-diphenylbutane-2,3-diol with DMSO-d₆.

To measure the environmental impact and the sustainability of the developed catalytic procedure we calculated the environmental (E) factor.²⁷ This green chemistry metric quantifies the ratio of the mass of waste per unit of product. The E factor for the oxidative cleavage of 2,3-diphenylbutane-2,3-diol, selected as model, under the optimized microwave heating conditions is 50.1 (including the organic solvent employed for the extraction). Notably, the E factor calculated for the same substrate under the recycling conditions (Scheme 1), where the amount of solvent employed for the extraction was optimized, dropped to 11.2.²⁸ These values are in the range of typical E factors of processes in fine-chemical companies and pharmaceutical industries.²⁹

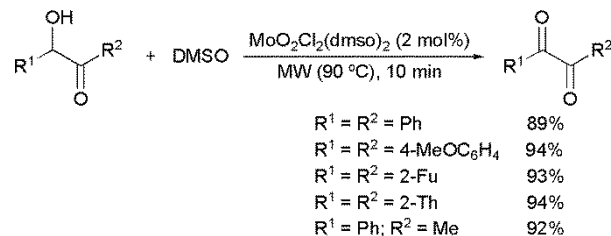
On the other hand, considering that α -hydroxyketones (acyloins) could be intermediates in the oxidative cleavage of secondary glycols under our catalytic conditions, we studied the reaction of benzoin (PhC(O)CH(OH)Ph) with DMSO and MoO₂Cl₂(dmsO)₂ (2 mol%) (microwave irradiation at 130 °C). The selective oxidation of the hydroxyl group, affording benzil (PhCOCOPh) in high yield, was observed without any cleavage of the molecule. This fact indicates that the oxidative cleavage of glycols under this catalytic system does not likely take place through the corresponding acyloins, but more probably involving a catalytic cycle such as that shown below (Scheme 2).



Scheme 2 Proposed catalytic cycle for the molybdenum-catalyzed oxidative cleavage of glycols

First, the molybdenum catalyst $\text{MoO}_2\text{Cl}_2(\text{dmsO})_2$ reacts with the glycol giving rise to the diolate complex **I** and water. The condensation of water from one of the oxo ligands on oxovanadium(V), oxomolybdenum(VI) or oxorhenium(VII) complexes and two hydrogen atoms from alcohols is well established.³⁰ At this point, oxidative cleavage of the glycolate ligand by the Mo(VI) center leads to the monoxomolybdenum(IV) species **II**, which possesses one or two weakly coordinated carbonyl derivatives.³¹ DMSO from the solution would displace the carbonyl compounds, affording an intermediate Mo(IV) species **III** that regenerates the catalyst releasing dimethyl sulfide as byproduct. So, the overall process involves the oxidative cleavage of the glycol by DMSO generating one molecule of water and dimethyl sulfide as the only wastes.

Nevertheless, considering that 1,2-diketones are important building blocks and that the development of clean methodologies for the selective oxidation of acyloins to diketones remains deserving interest in organic synthesis,³² we re-optimized the reaction conditions finding that the temperature could be reduced to 90 °C allowing the completion of the process in 10 min.³³ Then, we applied our developed methodology for the oxidation of a variety of acyloins, and this new procedure for the oxidation of α -hydroxyketones proved to be general for aryl, heteroaryl, or methyl substituted substrates, giving rise in all cases to the corresponding 1,2-diketones in almost quantitative yields (Scheme 3).



Scheme 3 Mo-catalyzed oxidation of acyloins with DMSO

Conclusions

In summary, we have developed an efficient catalytic methodology for the oxidative cleavage of 1,2-diols that could provide an attractive alternative in terms of green chemistry to the more extended Criegee and Malaprade reactions. The reported strategy employ easily available and environmentally friendly $\text{MoO}_2\text{Cl}_2(\text{dmsO})_2$ as catalyst and economical and non-toxic DMSO as oxidant. The reactions are performed in air and the products are easily isolated by a simple extraction that also allows catalyst recycling. Notably, a broad substrate scope for this transformation has been established, including disubstituted glycols that could be efficiently cleaved without overoxidation to the corresponding carboxylic acids. In addition, we have shown that the combination DMSO/Mo(VI) is useful as well for the selective transformation of acyloins in 1,2-diketones. The development of environmentally friendly protocols using low-toxic stoichiometric oxidants, such as DMSO, for the oxidative cleavage of related substrates, including biomass-derived feedstocks, is currently in progress.

Acknowledgements

We are grateful to the Ministerio de Economía y Competitividad (MINECO) and FEDER (CTQ2013-48937-C2-1-P) and Junta de Castilla y León (BU237U13) for financial support. R. R.-P. thanks Universidad de Burgos (UBU) for a predoctoral contract. P. G.-G. thanks MINECO for a Ramón y Cajal contract.

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- 32 $\text{MoOCl}_2(\text{dmsO})_2(\text{R}^1\text{R}^2\text{CO})$ (**II**) or, alternatively, seven-coordinated $\text{MoOCl}_2(\text{dmsO})_2(\text{R}^1\text{R}^2\text{CO})_2$, only likely exists at the precise moment of its formation as the displacement of the $\text{R}^1\text{R}^2\text{CO}$ by DMSO will be almost instantaneous.
- 33 (a) M. Kirihara, Y. Ochiai, S. Takizawa, H. Takahata and H. Nemoto, *Chem. Commun.* 1999, 1387–1388; (b) S. A. Tymonko, B. A. Nattier and R. S. Mohan, *Tetrahedron Lett.* 1999, **40**, 7657–7659; (c) Y. Shimakawa, T. Morikawa and S. Sakaguchi, *Tetrahedron Lett.* 2010, **51**, 1786–1789; (d) P. Muthupandi and G. Sekar, *Tetrahedron Lett.* 2011, **52**, 692–695; (e) J. M. Khurana, A. Chaudhary and S. Kumar, *Org. Prep. Proc. Int.* 2013, **45**, 241–245.
- 34 Lower temperatures led to slower reactions: ~66% of conversion was observed at 70 °C (10 min). Moreover, no reaction took place at 90 °C (10 min) without catalyst.