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Metal catalyzed oxidations. Part 2. Molybdenum catalyzed olefin epoxidation in nonpolar solvents [1]

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Abstract

2-(1-Octadecyl-3-pyrazolyl)pyridineoxodiperoxomolybdenum(VI) (**1**) is an active catalyst for olefin epoxidation. Due to its long alkyl side chain, it allows the reaction to be carried out in hydrocarbon solution. Epoxidations of several olefins with different functional groups are presented and discussed.

Keywords: Olefin; Epoxidation; Peroxo complexes; Molybdenum

1. Introduction

The epoxidation of olefins, followed by ring opening with various nucleophiles, is a key step in the synthesis of both, organic bulk chemicals and fine chemicals, pharmaceuticals, etc.. The direct epoxidation with oxygen is only known for ethylene [2]. Higher epoxides are generally obtained by the reaction of an olefin with a peroxidic compound. Percarboxylic acids, especially peracetic acid and *m*-chloro perbenzoic acid, are normally used in organic synthesis as stoichiometric oxidants [3]. Hydrogen peroxide and alkyl hydroperoxides are activated catalytically by high valent metal compounds [4]. All these systems stringently depend on special reaction conditions like temperature, polar solvents, pH value, etc.. Therefore the yields of sensitive epoxides, especially epoxides of small olefinic rings or high substituted olefins, are low due to ring opening reactions.

In this paper we present new molybdenum catalysts, which allow olefin epoxidations to be carried out in nonpolar and aprotic hydrocarbon solutions. The positive effects of our catalyst design are enhanced selectivity (epoxide vs. diol) combined with high reactivity.

2. Results and discussion

Transition metal complexes of titanium, molybdenum, tungsten, and rhenium are known to be catalytically active in olefin epoxidation. Quite a number of high and low valent molybdenum complexes like $Mo(CO)_6$, $MoO_2(acac)_2$, or molybdenum clusters [5] are used as catalysts. The most frequently tested systems are molybdenum oxobisperoxo complexes of type **A** (L = HMPT, pyridine, etc.) [4,6] and **B** (L–L = 2,2′-bipyridine, pyridine carboxylate, etc.) [7,8] (Scheme 1).

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[1] For Part 2 of the series: see [1].

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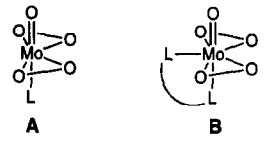


A B

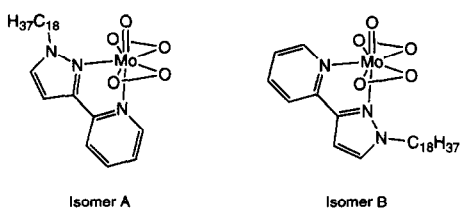
Scheme 1.

While six-coordinate complexes (Type **A**) are used as stoichiometric oxidants in halogenated hydrocarbons, most of the seven-coordinate complexes (Type **B**) are insoluble in organic solvents. Only pyridine carboxylates with tetraalkyl ammonium cations as counterions are sufficiently soluble in polar organic solvents, but due to the decreased Lewis acidity of the metal centre, these complexes show low catalytic activity in olefin epoxidation [8].

As we have shown previously, pyrazolyl pyridines substituted with alkyl side chains form soluble molybdenum oxobisperoxo complexes. These complexes are high active catalysts (TOF $[\text{moles}_{\text{substr}}/(\text{moles}_{\text{cat}} \cdot \text{h})] > 1500$ at 65°C) for the epoxidation of cyclooctene with *tert*-butyl hydroperoxide (TBHP) in chloroform [1]. The ligands are available via alkylation of deprotonated pyrazolyl pyridine with an alkyl halide in THF. The corresponding molybdenum complexes are formed in almost quantitative yield by adding a methanolic ligand solution to a solution of MoO_3 in H_2O_2. They are obtained as a mixture of two isomers A and B, which can be distinguished spectroscopically.

The octadecyl derivative **1** (Scheme 2) is soluble in toluene as well as in alkanes (isooctane: ca. 100 mg/ml) at temperatures above 50°C. We investigated the epoxidation of a number of olefins in these solvents, with particular regard to the stability of sensitive epoxides.

The epoxidations were carried out in 10 ml sure seal crimp capped glass vials at 100°C with an olefin/TBHP ratio of about 1.0/1.1 (Experimental part). We determined the conversion of the olefins after 1 h reaction time by GC analysis.



Isomer A Isomer B

1

Scheme 2.

2.1. *Unfunctionalized cyclic and linear monoolefins*

The epoxidations of cyclic and linear monoolefins lead to the corresponding epoxides in generally high yields (Table 1).

More electron-rich cyclic and multiple substituted linear olefins are obtained in higher yields. Terminal linear olefins can be almost quantitatively converted into the corresponding epoxides after a reaction time of 3 h. Epoxycyclopentane and 2,3-epoxy-2,3-dimethylbutane, which are notoriously sensitive against attack of nucleo- and electrophiles, are available in high yields. A large scale epoxidation of cyclopentene (50 g) in isooctane/TBHP, catalyzed by **1**, gave about 65% of epoxycyclopentane (Experimental part). These positive results can be explained by two properties of our catalytic system: Firstly, traces of water in the TPHP solution can be easily and completely removed with dry $MgSO_4$. Secondly, the chelating ligand reduces the Lewis acidity of the metal centre and therefore its potential to activate epoxides for ring opening reactions. We did not observe

Table 1
Epoxidation of unfunctionalized cyclic and linear olefins

Olefin	Yield (%) of epoxide after 1 h [a]		Remarks
	in toluene	in isooctane	
cyclooctene	100	95	
cyclohexene	93	93	
cyclopentene	87	100	
1-octene	55	58	
2-octene	96	81	
1-decene	54	55	
2,3-dimethyl-2-butene	74	87	epoxide
	18	traces	1,2-diol
	8	traces	pinacolone
2,4,4-trimethyl-2-pentene	98	88	+1,2-diol

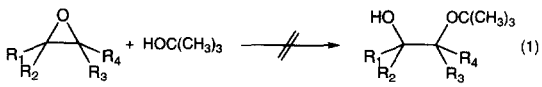
[a] Reaction conditions: ca. 10 mg (17 μmol) catalyst, ca. 1 ml olefin, 1.1 equiv. TBHP, 5 ml solvent, $T = 100$°C.

Table 2
Epoxidation of functionalized olefins and polyolefins

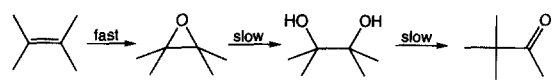
Olefin	Yield (%) of epoxide after 1 h [a]		Remarks
	in toluene	in isooctane	
mesityloxide (4-methyl-3-pentene-2-one)	40	39	
ethyl crotonate	<5	0	
allylphenyl ether	5	0	
styrene	21	57	styrene oxide
	12	18	*t*-butyl benzoate
2,3-dimethyl-butadiene	63	69	monoepoxide
	<5	<5	diepoxide
cyclooctatetraene	30	0	monoepoxide
cyclopentadiene (cp)	10	0	1,2-epoxycyclopent-3-ene
	16		epoxides of $(cp)_2$

[a] Reaction conditions: ca. 10 mg (17 μmol) catalyst, ca. 1 ml olefin, 1.1 equiv. TBHP, 5 ml solvent, $T = 100°C$.

formation of a 1-*tert*-butoxy-2-hydroxy alkane, the product of a ring opening reaction of an epoxide and *tert*-butanol, in any case (Eq. 1):



In addition, the reduced Lewis acidity of **1** is confirmed by the remarkably slow conversion of 1,2-dimethyl-1,2-butandiol into pinacolone at 100°C (Eq. 2):



(2)

2.2. *Functionalized olefins and polyolefins*

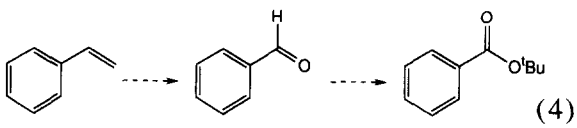
The rate of conversion of donor functionalized olefins depends clearly on the functionality of the substrates (Table 2).

While the conjugated enone mesityloxide (4-methyl-3-pentene-2-one) is converted into its epoxide in moderate yield (Eq. 3),

(3)

ated esters and allylic alcohols are not epoxidized. In our opinion, these more Lewis basic substrates decrease the Lewis acidity of the metal centre of **1** by coordination. They therefore decrease the activity of the catalyst in the same way as it is decreased by Lewis basic solvents like alcohols, ethers, esters, nitriles, etc..

Styrene is converted into the corresponding epoxide in quite good yields in isooctane solution. We found small amounts of *tert*-butyl benzoate, which should be formed from benzoic acid and *tert*-butanol. Benzoic acid is the final oxidation product in a reaction series starting with a C–C bond cleavage, either of styrene or epoxystyrene. One of the intermediates is benzaldehyde, which was detected in traces by GC/MS analysis (Eq. 4):



(4)

imethylbutadiene is selectively converted into the monoepoxide (only traces of diepoxide). This observation can be explained by a deactivation of the remaining C=C double bond by the epoxy function. The yield is high, after 3 h it is almost quantitative. Exclusive formation of a monoepoxide is observed in the case of cyclooctatetraene, too.

1,2-Epoxycyclopent-3-ene [9], the monoepoxide of cyclopentadiene, is an interesting starting material for the synthesis of prostaglandines [10].

It is very sensitive against ring opening. The apolar oxidation system we present here seemed promising to establish a new synthetic route for this compound. We obtained 1,2-epoxycyclopent-3-ene in low yields only. The reaction conditions (100°C) lead to formation of dicyclopentadiene by Diels–Alder reaction. As dicyclopentadiene is a substrate for catalytic epoxidation as well, two new products with molecular mass $M_m = 146$ are formed in almost equimolar ratio (Eq. 5):

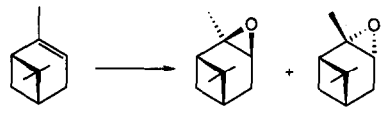
(5)

steric effects, only the exo diastereomers 2,3-epoxy-4,7-methylene-4,7,8,9-tetrahydroindene (**A**) and 5,6-epoxy-4,7-methylene-4,7,8,9-tetrahydroindene (**B**) should be formed. The mass spectra of both compounds are quite similar. The only differences are two intensive peaks ($m/z = 81$, 82) in the spectrum of **A**. They can be assigned to 1,2-epoxycyclopent-3-ene, which is formed by retro-Diels–Alder reaction under MS conditions. The diepoxide of dicyclopentadiene is formed only in traces at the given reaction conditions. Epoxidation of dicyclopentadiene followed by retro-Diels–Alder reaction, might therefore open a new access to 1,2-epoxycyclopent-3-ene and its derivatives.

2.3. Chiral olefins

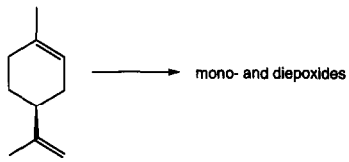
Epoxidation of chiral olefins either leads to pure enantiomers or to a mixture of diastereomers. Investigations on the diastereoselectivity of the catalytic system prooved that only slight diastereomeric excesses are produced under the given reaction conditions (Table 3).

The sterically hindered (1*R*)-(+)-α-pinene gives both diastereomeric α-pinene oxides in only 14 and 10% yield resp. Due to steric demands the *trans* compound should be the major product (Eq. 6):



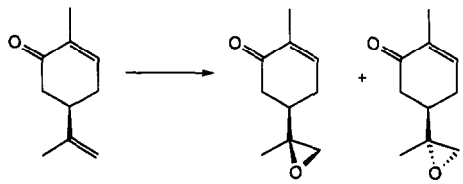
(6)

C=C double bonds of (*R*)-(+)-limonene are attacked unspecifically and a mixture of different diastereomeric mono- and diepoxides is formed (Eq. 7):



(7)

poxidation of (*R*)-(−)-carvone gives a 1:1 mixture of both diastereomeric exocyclic epoxides. The conjugated endocyclic double bond is not attacked (Eq. 8):



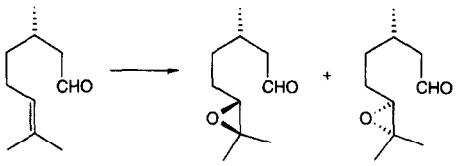
(8)

R)-(+)-Citronellal is converted into a 1:1 mixture of two diastereomeric epoxides. The aldehyde function remains intact (Eq. 9):

Table 3
Epoxidation of chiral olefins

Olefin	Yield (%) of epoxide after 1 h [a]		Remarks
	in toluene	in isooctane	
(1*R*)-(+)-α-pinene	24	0	2 diastereomers
(*R*)-(+)-limonene	100	68	various epoxides
(*R*)-(−)-carvone	67	65	2 diastereomers
(*R*)-(+)-citronellal	71	76	2 diastereomers

[a] Reaction conditions: ca. 10 mg (17 μmol) catalyst, ca. 1 ml olefin, 1.1 equiv. TBHP, 5 ml solvent, $T = 100$°C.



(9)

In summary it may be said that chiral olefins form mixtures of diastereomeric epoxides at the given reaction conditions. A decrease of reaction temperature will definitely decrease the rate of conversion but it might give us a chance to obtain one of the diastereomers exclusively. We are now working on the optimization of the reaction conditions, especially with regard to enantioselective epoxidations.

3. Conclusion and perspectives

We proved that long chain derivatives of pyrazolyl pyridines are suitable ligands for catalysts of type (L–L)$MoO(O_2)_2$ for the epoxidation of olefins in nonpolar solvents. Particularly sensitive epoxides are obtained in high yields as, due to a decreased Lewis acidity of the molybdenum centre, ring opening reactions are suppressed.

The work of Sharpless [11] and Jacobsen [12] demonstrates the synthetic potential of enantioselective olefin epoxidations with chiral titanium and manganese complexes. Chiral derivatives of pyrazolyl pyridines are known [13] and enantioselective epoxidations with chiral molybdenum peroxo complexes (ee < 35%) are already described in the literature [14]. Our next objective on molybdenum peroxo chemistry will therefore be an application of these complexes for enantioselective olefin epoxidations.

4. Experimental

4.1. General

The synthesis of the catalyst was carried out as described elsewhere [1]. We used a Hewlett-Packard HP 5890 gas chromatograph (capillary column: HP-1, 30 m, I.D. 0.25 mm; column head pressure: 50 kPa; temperature program: 60°C, 4 min, 15°C/min, 120°C, 2 min, 35°C/min, 240°C, 7 min) coupled with a HP 5970 mass selective detector for GC/MS characterization of catalytic epoxidation reactions. The preparation of dry *tert*-butyl hydroperoxide (TBHP) solutions started from commercially available TBHP, either in water (Aldrich, 18,471-3) or isooctane (2,2,4-tetramethylpentane; Aldrich, 33,127-9). Chloroform solutions were obtained by extracting aqueous solutions of TBHP with chloroform. Organic solutions of TBHP were dried twice, first with commercially available $MgSO_4$, second with extra dry $MgSO_4$ (200°C, 24 h), to remove any traces of water. The content of TBHP was determined by titration [15].

4.2. Catalytic olefin epoxidation

(A) In toluene: 10 mmol olefin, 5 ml toluene and 10 mg (17 μmol) **1** were mixed in a 10 ml crimp cap vial. After the vial was closed by a Sure Seal crimp cap, 2.3 ml (11 mmol) of a 4.7 M solution of TBHP in $CHCl_3$ were added via a syringe. The solution was stirred magnetically, heated to 100°C for 1 h and subsequently analyzed by GC/MS.

(B) In isooctane: 10 mmol olefin and 10 mg (17 μmol) **1** were mixed in a 10 ml crimp cap vial. After the vial was closed by a Sure Seal crimp cap, 2.5 ml (11 mmol) of a 4.5 M solution of TBHP in isooctane were added via a syringe. The solution was stirred magnetically, heated to 100°C for 1 h and subsequently analyzed by GC/MS.

4.3. Synthesis of epoxycyclopentane

In a 500 ml flask, equipped with a reflux condenser, 50.0 g (65 ml, 734 mmol) cyclopentene, 180 ml (807 mmol) of a 4.5 M solution of TBHP in isooctane and 0.72 g (1.25 mmol) (**1**) were heated to reflux for 3 h. The product was purified by distillation over a Vigreux column (bp.: 100–104°C). Yield: 40.0 g (65%) epoxicyclopentane (95% pure by GC).

Acknowledgements

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References

[1] W.R. Thiel, M. Angstl and T. Priermeier, Chem. Ber., 127 (1994) 2373.

[2] Ullmann's Enzyclopedia of Industrial Chemistry, Vol. A10, VCH Verlagsgesellschaft mbH, Weinheim, 1987, p. 117–135.

[3] E. Müller (Ed.), Methoden der organischen Chemie (Houben-Weyl), Vol. VI/3, 4th Ed., Georg Thieme Verlag, Stuttgart, 1965, p. 385–397.

[4] Reviews: (a) G. Strukul (Ed.), Catalytic Oxidations with Hydrogen Peroxide as Oxidant, Kluwer Academic Publishers, Rotterdam, 1992. (b) K.A. Jørgensen, Chem. Rev., 89 (1989) 431. (c) W.J. Mijs and C.H.R.I. de Jonge (Eds.), Organic Synthesis by Oxidation with Metal Compounds, Plenum Press, New York, 1986. (d) R.A. Sheldon and J.A. Kochi, Metal Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981. (e) R.A. Sheldon, in S. Patai (Ed.), The Chemistry of Peroxides, Wiley, New York, 1983, p. 161.

[5] (a) R.A. Sheldon and J.A. van Doorn, J. Catal., 31 (1973) 427. (b) R.A. Sheldon, J.A. van Doorn, C.W. Schram and H. de Jong, J. Catal., 31 (1973) 438. (c) B.M. Trost and Y. Masuyama, Isr. J. Chem., 24 (1984) 134.

[6] (a) H. Mimoun, I. Serée de Roch and L. Sajus, Tetrahedron, 26 (1970) 37. (b) V. Conte, F. Di Furia and G. Modena, J. Org. Chem., 53 (1988) 4581. (c) F.P. Ballistreri, S. Failla, E. Spina and G.A. Tomaselli, J. Mol. Catal., 50 (1988) 39. (d) A. Arcoria, F.P. Ballistreri, G.A. Tomaselli, F. Di Furia and G. Modena, J. Mol. Catal., 24 (1984) 189.

[7] (a) E.O. Schlemper, G.N. Schrautzer, and L.A. Hughes, Polyhedron, 3 (1984) 377. (b) W.A. Herrmann, W.R. Thiel and J.G. Kuchler, Chem. Ber., 123 (1990) 1953. (c) W.A. Herrmann, W.R. Thiel, J.G. Kuchler, J. Behm and E. Herdtweck, Chem. Ber., 123 (1990) 1963.

[8] S. Campestrini, F. Di Furia, P. Rossi, A. Torboli and G. Valle, J. Mol. Catal., 83 (1993) 95.

[9] M. Korach, D.R. Nielsen and W.H. Rideout, Organic Synthesis, Collective Volume V, Wiley, New York, 1973, p. 414.

[10] (a) review: P.W. Collins and S.W. Djuric, Chem. Rev., 93 (1993) 1533. (b) G. Stork and M. Isobe, J. Am. Chem. Soc., 97 (1975) 4745.

[11] (a) T. Katsuki and K.B. Sharpless, J. Am. Chem. Soc., 102 (1980) 5974. (b) B.E. Rossiter, T. Katsuki and K.B. Sharpless, J. Am. Chem. Soc., 103 (1981) 464. (c) V.S. Martin, S.S. Woodard, T. Katsuki, Y. Yamada, M. Ikeda and K.B. Sharpless, J. Am. Chem. Soc., 103 (1981) 6237.

[12] (a) W. Zhang, J.L. Loebach, S.R. Wilson and E.N. Jacobsen, J. Am. Chem. Soc., 112 (1990) 2801. (b) E.N. Jacobsen, W. Zhang, A.R. Muci, J.R. Ecker and L. Deng, J. Am. Chem. Soc., 113 (1991) 7063. (c) W. Zhang and E.N. Jacobsen, J. Org. Chem., 56 (1991) 2296.

[13] H. Brunner and T. Scheck, Chem. Ber., 125 (1992) 701.

[14] H.B. Kagan, H. Mimoun, C. Mark and V. Schurig, Angew. Chem., 91 (1979) 511; Angew. Chem., Int. Ed. Engl., 6 (1979) 485.

[15] Houben-Weyl: Methoden der organischen Chemie, Vol. E13, 4th Ed., Georg Thieme Verlag, Stuttgart, 1988, p. 1390.