An improved methyltrioxorhenium-catalyzed epoxidation of alkenes with hydrogen peroxide

Shigekazu Yamazaki*

Received 10th April 2007, Accepted 16th May 2007
First published as an Advance Article on the web 30th May 2007
DOI: 10.1039/b705276f

Methyltrioxorhenium (MTO)-catalyzed epoxidation of alkenes with H_2O_2 has been significantly improved by using 3-methylpyrazole as an additive. A system consisting of 35% H_2O_2 and MTO–3-methylpyrazole in CH_2Cl_2 catalyzes the epoxidation of various alkenes in excellent yields. The catalytic activity of MTO–3-methylpyrazole surpasses MTO–pyrazole and MTO–pyridine catalysts. Quantitative yields of epoxides from cyclic and internal alkenes were obtained with only 0.05–0.1 mol% of MTO in the presence of 10 mol% of 3-methylpyrazole.

Introduction

The epoxidation is an important transformation of alkenes, because epoxides are versatile intermediates in organic synthesis. The use of transition metal complexes as the epoxidation catalyst is of particular interest,[1] due to their ability to activate environmentally benign oxidants such as molecular oxygen[2] and H_2O_2.[3,4]

An important improvement in the field of catalytic epoxidation arose with the discovery of the catalytic activity of methyltrioxorhenium(VII) (CH_3ReO_3, MTO)[5] by Herrmann and co-workers in 1991.[6] MTO has emerged as one of the most active catalysts for alkene epoxidation in the presence of H_2O_2 as the terminal oxidant.

MTO-catalyzed epoxidation was initially investigated in a homogeneous medium using *tert*-BuOH as solvent with anhydrous H_2O_2.[6,7] While high yields of certain epoxides may be obtained by this procedure, the main disadvantage, however, was the low selectivity in the cases where acid sensitive epoxides were formed. The Lewis acidity of the rhenium center caused hydrolysis and concomitant cleavage of the epoxide ring leading to the formation of 1,2-diols in the presence of water.[7]

Several methods have been suggested to overcome this problem. Herrmann and co-workers have reported that addition of a Lewis base ligand, *e.g.*, quinuclidine, pyridine and its derivatives, suppresses the epoxide ring-opening process by reducing the Lewis acidity of the rhenium center.[7] However, while the selectivity toward epoxides increases, the conversion of the activity of the catalytic system decreases.

Use of a urea–H_2O_2 complex instead of aqueous H_2O_2 was examined to overcome the formation of diols, and somewhat improved the substrate scope of the system.[8]

A major improvement in the MTO-catalyzed epoxidation was achieved by Sharpless and co-workers.[9] They have reported that a biphasic system (aqueous phase/organic phase) and addition of a significant excess of an aromatic monodentate Lewis base, such as pyridine, relative to the catalyst not only suppresses the ring opening but also accelerates the alkene epoxidation in comparison to MTO itself.[10–12]

Shortly afterwards new improvements were achieved by the groups of Sharpless[13a] and Herrmann.[14a] It was found that the use of 3-cyanopyridine and especially pyrazole as the Lewis base is more effective and less problematic than the use of pyridine, since the latter ligand can be easily oxidized to its N-oxide, which is a less efficient ligand.[10]

Herein we wish to report an improved method of MTO-catalyzed epoxidation. We have found 3-methylpyrazole as an additive to be a more suitable ligand than pyridine and pyrazole for this catalytic epoxidation. The use of 3-methylpyrazole enhances the rate of epoxidation while reducing the amount of MTO.

Results and discussion

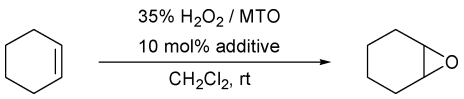
Herrmann and co-workers investigated some pyrazole derivatives as additives for MTO-catalyzed epoxidation of styrene, and concluded that 3-methylpyrazole was less effective than pyrazole.[14a] During our research on the effect of additives for the MTO-catalyzed epoxidation, we have found that 3-methylpyrazole is a superior additive than pyrazole for epoxidation of some types of alkenes.

In order to evaluate the efficiency of 3-methylpyrazole as the additive, we compared pyridine, pyrazole and 3-methylpyrazole in MTO-catalyzed epoxidation of cyclohexene. The results are summarized in Table 1.

When the epoxidation of cyclohexene was carried out with 0.2 mol% MTO, the reaction using 3-methylpyrazole as an additive was completed within 1 h (entry 5), while the reactions using pyridine and pyrazole were completed at 5 h and 3 h respectively (entries 1 and 3). The reaction time of MTO–3-methylpyrazole is remarkably shorter than those of the other MTO–ligand catalysts. When the amount of MTO was reduced to 0.1 mol%, the reaction using 3-methylpyrazole was completed within 4 h (entry 6), while the reactions using pyridine and pyrazole were not completed within 5 h (86% conversion in both cases, entries 2 and 4). In the case of 3-methylpyrazole, the reduced amount of MTO (0.05 mol%, entry 7) afforded 96% epoxide at 5 h. The addition of 4-methylpyrazole was also effective. The epoxidation of cyclohexene with 0.1 mol% MTO in the presence of

Toyama Industrial Technology Center, 150 Futagami, Takaoka, Toyama, 933–0981, Japan. E-mail: s-yamazk@itc.pref.toyama.jp.; Fax: +81-766-21-2402; Tel: +81-766-21-2121

Table 1 MTO-catalyzed epoxidation of cyclohexene with 35% H_2O_2[a]



Entry	Additive	MTO (mol%)	Time/h	Convn[b] (%)	Epoxide[b] (%)
1	Pyridine	0.2	5	99	>99
2	Pyridine	0.1	5	86	>99
3	Pyrazole	0.2	3	>99	>99
4	Pyrazole	0.1	5	86	>99
5	3-MePz[c]	0.2	1	>99	>99
6	3-MePz[c]	0.1	4	>99	>99
7	3-MePz[c]	0.05	5	96	>99
8	4-MePz[d]	0.1	4	>99	>99
9	4-MePz[d]	0.05	5	90	>99

[a] Cyclohexene (20 mmol), 35% H_2O_2 (40 mmol), additive (2 mmol), in CH_2Cl_2 (10 mL) at room temperature. [b] Determined by GC analysis. [c] 3-Methylpyrazole. [d] 4-Methylpyrazole.

4-methylpyrazole resulted in complete conversion of cyclohexene to epoxide (entry 8). Fig. 1, the reaction profile of cyclohexene epoxidations, shows that the epoxidation with 0.1 mol% MTO using 3-methylpyrazole was faster than those using pyridine and pyrazole. The results in Table 1 and Fig. 1 clearly indicated that 3-methylpyrazole is a superior additive than pyridine and pyrazole for MTO-catalyzed epoxidation of cyclohexene.

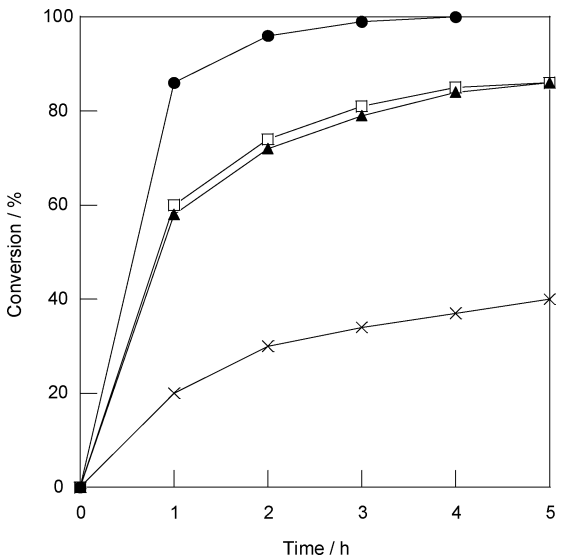


Fig. 1 Time course of MTO-catalyzed epoxidation of cyclohexene. Conditions: cyclohexene (20 mmol), 35% H_2O_2 (40 mmol), MTO (0.02 mmol), additive (2 mmol), in CH_2Cl_2 (10 mL) at room temperature. Analysis by GC. (●) Curve A: 3-methylpyrazole. (▲) Curve B: pyrazole. (□) Curve C: pyridine. (×) Curve D: no additive.

The MTO-catalyzed epoxidation of cyclohexene with 0.2 equivalent of H_2O_2 afforded cyclohexene oxide in 20% yield (100% based on H_2O_2 consumed). The epoxidation of cyclohexene with 1.1 equivalent of H_2O_2 resulted in complete conversion of the alkene to the epoxide. These results indicated that this epoxidation proceeded with high efficiency of H_2O_2 utilization and with high selectivity to the epoxides.

The results of MTO-catalyzed epoxidation for a variety of alkenes using 3-methylpyrazole as the additive are summarized in Table 2. In the cases of cyclic alkenes (entries 1, 3, 5, 7, 9, and 14), the alkenes were converted to epoxides quantitatively with only 0.1 mol% MTO at reasonable reaction times. No ring-opening or oxidative-cleavage by-products were observed in these cases. Complete conversions of cyclic alkenes to epoxides were also observed with reduced amount of MTO (0.05 mol%) with longer reaction times (entries 2, 4, 6, 8, 10, and 15). Cyclooctene can be converted to cyclooctene oxide quantitatively with only 0.02 mol% MTO within 24 h (entry 11). The turnover numbers (TON) of cyclooctene epoxidation with pyridine, pyrazole, and 3-methylpyrazole were compared at a catalyst concentration of 0.01 mol% (Table 3). The epoxidation with 3-methylpyrazole exhibited the highest TON of 7200. At catalyst concentration of 0.001 mol% of MTO, the conversion at 6 h was 20%, which represents a TON of 20000 (Table 2, entry 13). This is the best TON reported to date on MTO-catalyzed epoxidation.[15a] The internal alkenes such as *trans*- and *cis*-2-octene were also converted to epoxides quantitatively with 0.1 mol% MTO at reasonable reaction times (entries 27, 28, 29, and 30).

The epoxides of substituted styrenes are known to be very prone to ring-opening and rearrangement reactions. With this additive, styrene, α-methylstyrene, *cis*- and *trans*-β-methylstyrene were also converted to their epoxides in excellent yields (entries 16, 17, 20, 21, 22, 23, and 24). The addition of either pyrazole or 3-methylpyrazole in styrene epoxidation resulted in almost same outcome (entries 16 and 18), while pyridine had an inferior effect (entry 19).[9,13,14] In the case of styrene epoxidation, small amounts of styrene glycol (2%) and benzaldehyde (1%) were also detected (entry 16).

Functional groups such as alcohols and esters do not interfere with the epoxidation reaction and good yields were obtained (entries 32–36).

Although aliphatic terminal alkenes, such as 1-hexene and 1-octene, were epoxidized slower than cycloalkenes and styrenes, the alkenes were converted to epoxides over 90% yields within 8 h with 0.5 mol% MTO (entries 25, 26, and 31). The time courses of the epoxidation of 1-octene by MTO–3-methylpyrazole, MTO–pyrazole, and MTO–3-cyanopyridine[13] are shown in Fig. 2. These

Table 2 MTO-Catalyzed epoxidation of various alkenes with 35% H_2O_2 in the presence of 3-methylpyrazole in CH_2Cl_2[a]

Entry	Alkene	MTO (mol%)	Temperature/°C	Time/h	Conversion[b] (%)	Epoxide[b] (%)
1	1-Methylcyclohexene	0.1	10	5	>99	>99
2	1-Methylcyclohexene	0.05	10	24	99	>99
3	1-Phenylcyclohexene	0.1	rt	3	>99	95
4	1-Phenylcyclohexene	0.05	rt	8	97	96
5	Cyclopentene	0.1	rt	2.5	>99	>99
6	Cyclopentene	0.05	rt	6	99	>99
7	Cycloheptene	0.1	rt	3	>99	>99
8	Cycloheptene	0.05	rt	7	99	99
9	Cyclooctene	0.1	rt	2	>99	>99(91)[c]
10	Cyclooctene	0.05	rt	4	>99	>99
11	Cyclooctene	0.02	rt	24	99	>99
12	Cyclooctene	0.01	rt	6	72	>99
13	Cyclooctene	0.001	rt	6	20	>99
14	Norbornene	0.1	rt	2.5	>99	>99
15	Norbornene	0.05	rt	24	>99	>99
16	Styrene	0.5	rt	4	>99	97[d]
17	Styrene	0.2	rt	5	92	99
18	Styrene	0.5[d]	rt	5	>99	96
19	Styrene	0.5[f]	rt	5	66	99
20	α-Methylstyrene	0.1	rt	3	95	97
21	*trans*-β-Methylstyrene	0.1	rt	5	>99	>99[g]
22	*trans*-β-Methylstyrene	0.05	rt	24	>99	>99[g]
23	*cis*-β-Methylstyrene	0.1	rt	5	>99	>99[h]
24	Indene	0.2	rt	1	98	89
25	1-Hexene	0.5	rt	8	94	96
26	1-Octene	0.5	rt	8	98	93
27	*trans*-2-Octene	0.1	rt	6	>99	>99[g]
28	*cis*-2-Octene	0.1	rt	3	>99	>99[h]
29	*trans*-4-Octene	0.1	rt	8	98	>99[g]
30	*cis*-4-Octene	0.1	rt	5	99	>99[h]
31	1-Decene	0.5	rt	14	97	96
32	Cinnamyl alcohol	0.2	rt	5	>99	79
33	Cinnamyl acetate	0.5	rt	20	>99	95
34	Citronellol	0.1	10	4	>99	97
35	*trans*-2-Hexen-1-ol	0.2	rt	8	>99	>99[g]
36	*trans*-3-Hexen-1-ol	0.2	rt	7	>99	>99[g]

[a] Alkene (20 mmol), 35% H_2O_2 (40 mmol), 3-methylpyrazole (2 mmol), in CH_2Cl_2 (10 mL). [b] Determined by GC analysis. [c] Isolated yield by 10 g scale experiment. See Experimental section. [d] Styrene glycol (2%) and benzaldehyde (1%) were also produced. [e] Pyrazole (2 mmol) was used instead of 3-methylpyrazole. [f] Pyridine (2 mmol) was used instead of 3-methylpyrazole. [g] *trans*-Epoxide. [h] *cis*-Epoxide.

Table 3 Comparison of turnover numbers of MTO-catalyzed epoxidation of cyclooctene using various additives[a]

Entry	Additive	TON[b]
1	—	82
2	Pyridine	3960
3	Pyrazole	2300
4	3-Methylpyrazole	7200

[a] Cyclooctene (40 mmol), 35% H_2O_2 (80 mmol), MTO (0.004 mmol), additive (4 mmol), in CH_2Cl_2 (20 mL) at 20 °C for 6 h. [b] Turnover number at 6 h.

results indicated that the efficiency for epoxidation of terminal alkenes by these three catalytic systems is comparable.

The best results for MTO-catalyzed epoxidation in CH_2Cl_2 to date were reported with pyrazole as the Lewis base ligand (0.5 mol% MTO, pyrazole : MTO ratio of 24 : 1, in CH_2Cl_2).[14] The change of the solvent from CH_2Cl_2 to fluorinated alcohols such as trifluoroethanol[15a] and hexafluoro-2-propanol[15b] allowed reduction of the MTO loading to 0.1 mol%. However, acid-sensitive epoxides undergo ring-opening leading to a mixture of compounds in these fluorinated alcohols.[15] The use of 3-methylpyrazole will allow reduction of MTO loading to <0.1 mol% without changing the solvent from CH_2Cl_2 to fluorinated alcohols.

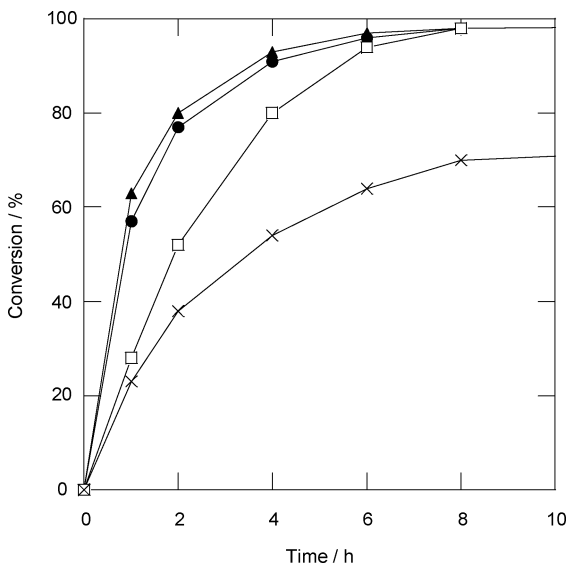


Fig. 2 Time course of MTO-catalyzed epoxidation of 1-octene. Conditions: 1-octene (20 mmol), 35% H_2O_2 (40 mmol), MTO (0.1 mmol), additive (2 mmol), in CH_2Cl_2 (10 mL) at room temperature. Analysis by GC. (●) Curve A: 3-methylpyrazole. (▲) Curve B: pyrazole. (□) Curve C: 3-cyanopyridine. (×) Curve D: no additive.

When reducing the amount of 3-methylpyrazole to 5 mol%, the rate of the cyclohexene epoxidation was somewhat slower than that for 10 mol% additive. The rates of the epoxidation using 10 mol% and 20 mol% additive were identical. As a result, addition of 10 mol% 3-methylpyrazole is required to obtain the best result, although 3-methylpyrazole does not react under the oxidation conditions as pyrazole.[14a]

The pK_a of 3-methylpyrazole is 3.3.[16] The value is higher than those of 3-cyanopyridine (pK_a 1.5) and pyrazole (pK_a 2.5), and is lower than that of pyridine (pK_a 5.2), namely 3-methylpyrazole has higher basicity than 3-cyanopyridine and pyrazole, and has lower basicity than pyridine. Adolfsson and co-workers reported[13c] MTO-catalyzed epoxidation of styrene with substituted pyridines of various pK_a. Among the pyridines examined, 3-chloropyridine (pK_a 2.8), 3-fluoropyridine (pK_a 3.0), methyl nicotinate (pK_a 3.3) and methyl isonicotinate (pK_a 3.3) that have similar pK_a values to 3-methylpyrazole allowed the reaction to reach high conversion (indicating long catalyst lifetime) with high selectivity of epoxide (conversion >90% and selectivity >90%). More basic pyridines (pyridine, 4-picoline pK_a 6.0, 4-*tert*-butylpyridine pK_a 6.0, 4-methoxypyridine pK_a 6.6) resulted in lower conversion (short catalyst lifetime) with excellent selectivity. The pyridines that are less basic (3-cyanopyridine, 4-cyanopyridine pK_a 1.9) exhibit quantitative conversion along with drastically low selectivity (<10% epoxide). The nitrogen heterocycles that have pK_a values about 2–4 may afford good balance of conversion and selectivity.

The presence of nitrogen heterocycles in the medium increases the concentration of the mono-hydrogen peroxide anion (HOO^-), which results in a faster formation of the peroxorhenium complexes from MTO. The higher concentration of HOO^- is also increasing the rate of MTO decomposition through a base-mediated pathway.[17,18] On the other hand, the coordination of heterocycles to MTO must protect the catalyst from deactivation by the base-mediated pathway. The concentration of HOO^- is higher and the formation of peroxo complexes is faster in the presence of 3-methylpyrazole than pyrazole, because the basicity of 3-methylpyrazole, which has an electron-releasing substituent, is higher than that of pyrazole. The basicity values of pyrazole and 3-methylpyrazole are not so high as that of pyridine, and the difference in MTO deactivation rates of these must be small. Although the origin of the rate-improving effect on MTO-catalyzed epoxidation with heterocycle additives is still not fully understood,[13c,17] these may be the reason for the higher reactivity and longer catalyst lifetime of 3-methylpyrazole than pyrazole.

Conclusions

We have explored and succeeded in enhancing the catalytic activity of MTO for epoxidation with 35% H_2O_2 by using a re-examined additive 3-methylpyrazole that has been found to be a superior additive to pyridine and pyrazole. The MTO–3-methylpyrazole system has the highest activity among MTO-based catalytic systems (MTO–pyrazole, MTO–pyridine, *etc.*) reported to date especially for epoxidation of cyclic and internal alkenes. Epoxides were obtained quantitatively from cyclic and internal alkenes with only 0.02–0.1 mol% MTO and 10 mol% 3-methylpyrazole without using highly concentrated H_2O_2 (>60%) and/or expensive fluorinated alcohols. On the other hand, the effects of 3-methylpyrazole and pyrazole were comparable in the epoxidation of terminal alkenes such as 1-octene and styrene. 3-Methylpyrazole is commercially available and would be the additive of choice for MTO-catalyzed epoxidation of a variety of alkenes. The continuous exploration of various amine compounds as additives will open perspectives for further enhancement of the catalytic activity of MTO.

Experimental

General remarks

All reagents obtained were from commercial sources unless otherwise noted and were used without further purification. Methyltrioxorhenium was prepared according to the reported procedure.[19] The concentration of hydrogen peroxide was determined by iodometric titration before use. The progress of the reaction was monitored by GC analysis. The conversions of alkenes and yields of epoxides were determined by the GC internal standard method. GC analyses were performed on a Shimadzu GC-2010 (FID detector) equipped with a GL Sciences InertCap 1 column (30 m length × 0.25 mm ID × 0.25 μm film thickness).

Typical procedures for epoxidations

Cyclohexene epoxidation (Table 1, entry 6). A 50 mL flask equipped with a stirbar was charged with CH_2Cl_2 (10 mL), 3-methylpyrazole (161 μL, 2.0 mmol, 10 mol%), MTO (5 mg, 0.020 mmol, 0.1 mol%), and cyclohexene (2.03 mL, 20 mmol). H_2O_2 (35%, 3.36 mL, 40 mmol) was added all at once to the stirring solution. The resulted two-phase mixture was stirred vigorously (1000 rpm) at room temperature. The progress of the reaction was monitored at appropriate intervals by GC analysis of small aliquots of the organic phase. The conversion of cyclohexene and yield of cyclohexene oxide were determined by the GC internal standard method. The GC internal standard material (*n*-undecane) was added just before the first analysis.

Procedure for 10 g scale epoxidation of cyclooctene (Table 2, entry 9). A 200 mL flask equipped with a stirbar was charged with CH_2Cl_2 (50 mL), 3-methylpyrazole (0.73 mL, 9.07 mmol, 10 mol%), MTO (22.6 mg, 0.0907 mmol, 0.1 mol%), and cyclooctene (10 g, 90.7 mmol). H_2O_2 (35%, 15.3 mL, 181 mmol) was added dropwise to the stirring solution from a dropping funnel (*ca.* 10 min). During the H_2O_2 addition the temperature of the solution was kept below 30 °C by applying an external cooling bath. The resulted two-phase mixture was stirred vigorously (1000 rpm) at room temperature. The reaction was completed after 2 h, and the reaction mixture was poured into brine. The aqueous layer was separated, and the remaining organic layer was washed with aqueous $Na_2S_2O_3$. The organic layer was successively washed with dilute HCl (2 mL 35% HCl with 50 mL H_2O) to remove 3-methylpyrazole. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was distilled out by using an evaporator. The residue was dried under vacuum. Cyclooctene oxide was obtained as a colorless solid (10.4 g, 91%, >98% purity by GC. The main impurity was cyclooctane that was contained in the starting alkene).

Notes and references

1 (*a*) R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981; (*b*) G. Strukul, *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, Kluwer Academic Publishers, New York, 1992; (*c*) C. W. Jones, *Application of Hydrogen Peroxide and Derivatives*, Royal Society of Chemistry, Cambridge, 1999; (*d*) W. Adam, *Peroxide Chemistry*, Wiley-VCH, Weinheim, 2000; (*e*) J.-E. Bäckvall, *Modern Oxidation Methods*, Wiley-VCH, Weinheim, 2004.

2 A review on epoxidation using O_2 as an oxidant: T. Mukaiyama and T. Yamada, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 17.

3 Reviews on epoxidation using H_2O_2 as an oxidant: (*a*) N. Mizuno and Y. Yamaguchi, *Chem. Rec.*, 2006, **6**, 12; (*b*) G. Grigoropoulou, J. H. Clark and J. A. Elings, *Green Chem.*, 2003, **5**, 1; (*c*) B. S. Lane and K. Burgess, *Chem. Rev.*, 2003, **103**, 2457.

4 Recent examples of efficient metal-catalyzed epoxidation using aqueous H_2O_2 see: (*a*) K. Sato, M. Aoki, M. Ogawa, M. Hashimoto, D. Panyella and R. Noyori, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 905; (*b*) M. C. White, A. G. Doyle and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2001, **123**, 7194; (*c*) K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi and N. Mizuno, *Science*, 2003, **300**, 964; (*d*) N. Gharah, S. Chakraborty, A. K. Mukherjee and R. Bhattacharyya, *Chem. Commun.*, 2004, 2630; (*e*) M. Klawonn, M. K. Tse, S. Bhor, C. Döbler and M. Beller, *J. Mol. Catal. A: Chem.*, 2004, **218**, 13.

5 Reviews on MTO-catalyzed oxidations: (*a*) J. H. Espenson, *Chem. Commun.*, 1999, 479; (*b*) G. S. Owens, J. Arias and M. M. Abu-Omar, *Catal. Today*, 2000, **55**, 317; (*c*) F. E. Kühn, A. Scherbaum and W. A. Herrmann, *J. Organomet. Chem.*, 2004, **689**, 4149.

6 W. A. Herrmann, R. W. Fischer and D. W. Marz, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1638.

7 W. A. Herrmann, R. W. Fischer, M. U. Rauch and W. Scherer, *J. Mol. Catal.*, 1994, **86**, 243.

8 (*a*) W. Adam and C. M. Mitchell, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 533; (*b*) T. R. Boehlow and C. D. Spilling, *Tetrahedron Lett.*, 1996, **37**, 2717.

9 J. Rudolph, K. L. Reddy, J. P. Chiang and K. B. Sharpless, *J. Am. Chem. Soc.*, 1997, **119**, 6189.

10 W. A. Herrmann, H. Ding, R. M. Kratzer, F. E. Kühn, J. J. Haider and R. W. Fischer, *J. Organomet. Chem.*, 1997, **549**, 319.

11 Aromatic bidentate Lewis bases, such as 2,2′-bipyridine, were also reported to suppress the ring-opening and accelerate the alkene epoxidation: (*a*) M. Nakajima, Y. Sasaki, H. Iwamoto and S. Hashimoto, *Tetrahedron Lett.*, 1998, **39**, 87; (*b*) H. Rudler, J. R. Gregorio, B. Denise, J. M. Brégeault and A. Deloffre, *J. Mol. Catal. A: Chem.*, 1998, **133**, 255; (*c*) P. Ferreira, W.-M. Xue, É. Bencze, E. Herdtweck and F. E. Kühn, *Inorg. Chem.*, 2001, **40**, 5834.

12 Recently synthesis of MTO Schiff-base complexes and their applications in olefin epoxidation has been reported: M.-D. Zhou, J. Zhao, J. Li, S. Yua, C.-N. Bao, J. Mink, S.-L. Zang and F. E. Kühn, *Chem.–Eur. J.*, 2007, **13**, 158.

13 (*a*) C. Copéret, H. Adolfsson and K. B. Sharpless, *Chem. Commun.*, 1997, 1565; (*b*) H. Adolfsson, A. Converso and K. B. Sharpless, *Tetrahedron Lett.*, 1999, **40**, 3991; (*c*) H. Adolfsson, C. Copéret, J. P. Chiang and A. K. Yudin, *J. Org. Chem.*, 2000, **65**, 8651.

14 (*a*) W. A. Herrmann, R. M. Kratzer, H. Ding, W. R. Thiel and H. Glas, *J. Organomet. Chem.*, 1998, **555**, 293; (*b*) F. E. Kühn, A. M. Santos, P. W. Roesky, E. Herdtweck, W. Scherer, P. Gisdakis, I. V. Yudanov, C. D. Valentin and N. Rösch, *Chem.–Eur. J.*, 1999, **5**, 3603.

15 The highest TON (2700, cyclohexene) on MTO-catalyzed epoxidation reported before this manuscript was obtained using a 60% H_2O_2/MTO/pyrazole/trifluoroethanol system: (*a*) M. C. A. van Vliet, I. W. C. E. Arends and R. A. Sheldon, *Chem. Commun.*, 1999, 821; (*b*) J. Iskra, D. Bonnet-Delpon and J.-P. Bégué, *Tetrahedron Lett.*, 2002, **43**, 1001.

16 J. Elguero, E. Gonzalez and R. Jacuier, *Bull. Soc. Chim. Fr.*, 1968, 5009.

17 W. D. Wang and J. H. Espenson, *J. Am. Chem. Soc.*, 1998, **120**, 11335–11341.

18 M. M. Abu-Omar, P. J. Hansen and J. H. Espenson, *J. Am. Chem. Soc.*, 1996, **118**, 4966.

19 W. A. Herrmann, F. E. Kühn, R. W. Fischer, W. R. Thiel and C. C. Romao, *Inorg. Chem.*, 1992, **31**, 4431.