

Methyltrioxorhenium-catalysed epoxidation of alkenes in trifluoroethanol

Michiel C. A. van Vliet, Isabel W. C. E. Arends and R. A. Sheldon*

Laboratory for Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands. E-mail: secretariat-ock@stm.tudelft.nl

Received (in Cambridge, UK) 17th March 1999, Accepted 30th March 1999

The well known methyltrioxorhenium-catalysed epoxidation of alkenes with aqueous H_2O_2 is significantly improved by conducting the epoxidation in trifluoroethanol; excellent reaction rates and yields can be obtained for a variety of (terminal) alkenes with only 0.1 mol% of catalyst.

Catalytic epoxidation of alkenes with aqueous H_2O_2 has been extensively studied in the last two decades.¹ Rhenium-based systems are especially interesting because rhenium, in contrast to many other transition metals, does not catalyse the facile decomposition of H_2O_2 .²

The discovery of the catalytic activity of methyltrioxorhenium (MeReO_3 ; MTO) by Herrmann and co-workers³ marks a turning point in the use of rhenium compounds as catalysts for epoxidations with H_2O_2 . This catalyst proved to be very active in epoxidation with anhydrous H_2O_2 in Bu^iOH . The main disadvantage, however, was the low selectivity when acid sensitive epoxides were formed. The high acidity of $\text{MTO-H}_2\text{O}_2$ caused hydrolysis and further degradation of the epoxide. This drawback could be partly circumvented by adding basic ligands (e.g. bipyridine) to the catalyst, but not without decreasing the activity of the catalyst.⁴

A major improvement in the MTO catalysed epoxidation was achieved by Sharpless and co-workers.⁵ They discovered that a large excess of pyridine relative to the catalyst (>10:1) actually improved the activity of the catalyst while maintaining the high selectivity. An important feature of this new system was the possibility of using commercially available aqueous H_2O_2 as the oxidant. This discovery boosted interest in MTO research and shortly afterwards new improvements were achieved by the Sharpless and Herrmann groups.^{6,7} The best results up to now were reported with pyrazole (pyrazole:MTO ratio of 24:1) as the basic ligand and CH_2Cl_2 as solvent.⁷

During our research on catalytic epoxidation with inorganic rhenium compounds as the catalyst, we found that trifluoroethanol was an excellent solvent for epoxidations with aqueous H_2O_2 .⁸ We subsequently found that a major improvement could be achieved when this solvent was used in the MTO system.

Fig. 1 shows the catalytic epoxidation of hex-1-ene. The results using 0.5 mol% MTO, 10 mol% pyrazole and 2 equiv. 30% H_2O_2 in CH_2Cl_2 are comparable to those reported by Herrmann and co-workers (95% conversion in 8 h; curve A). The use of 0.1 mol% MTO resulted in a much slower reaction and complete conversion of the alkene could not be reached in 24 h (curve B). The use of 60% H_2O_2 showed a slightly increased rate, but again complete conversion was not reached in 24 h (curve C).

A marked increase in the rate was observed, however, when the same catalyst and ligand were used in trifluoroethanol. This increase was observed both with 30% H_2O_2 (curve D) and more pronounced with 60% H_2O_2 (curve E). The rate was comparable to that observed with five times as much MTO in CH_2Cl_2 and complete conversion of the alkene with high selectivity to the epoxide could be reached within 24 h. With 5 mol% of pyrazole the rate was even slightly higher and a 95% yield of epoxide could be obtained in 5 h (curve F). The use of pyridine or

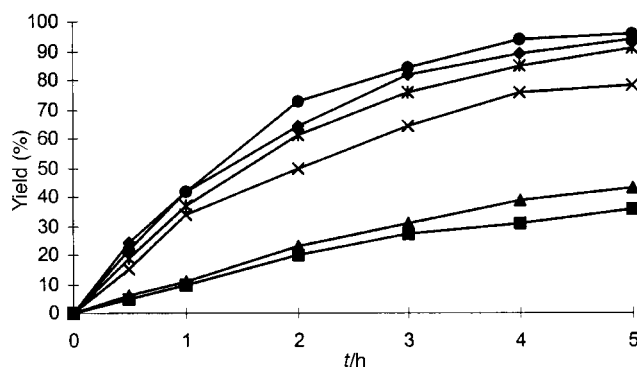


Fig. 1 Epoxidation of hex-1-ene by various catalytic systems. Conditions: 10 mmol hex-1-ene, 1 mmol Bu_2O (internal standard), MeReO_3 , pyrazole, 20 mmol H_2O_2 and 5 ml of solvent. Reaction at room temperature. Analysis by GC. (◆) Curve A: 0.5 mol% MTO, 10 mol% pyrazole, 30% H_2O_2 in CH_2Cl_2 . (■) Curve B: 0.1 mol% MTO, 10 mol% pyrazole, 30% H_2O_2 in CH_2Cl_2 . (▲) Curve C: 0.1 mol% MTO, 10 mol% pyrazole, 60% H_2O_2 in CH_2Cl_2 . (×) Curve D: 0.1 mol% MTO, 10 mol% pyrazole, 30% H_2O_2 in trifluoroethanol. (*) Curve E: 0.1 mol% MTO, 10 mol% pyrazole, 60% H_2O_2 in trifluoroethanol. (●) Curve F: 0.1 mol% MTO, 5 mol% pyrazole, 60% H_2O_2 in trifluoroethanol.

3-cyanopyridine resulted in slower rates, in analogy with the CH_2Cl_2 based system.

The high rates in trifluoroethanol are in agreement with earlier observation by Sharpless and co-workers, who found that polar, non-coordinating solvents showed the highest rates.⁵ Despite its alcoholic nature, trifluoroethanol is a non-coordinating solvent owing to the strong electron-withdrawing effect of the trifluoromethyl group. The trifluoromethyl group also prevents the oxidation of the alcohol group, rendering this primary alcohol relatively stable towards oxidation.

Based on these results we tested a number of terminal alkenes in the MTO catalysed epoxidation in trifluoroethanol (Table 1). In most cases complete conversion was observed within 24 h

Table 1 Epoxidation of terminal alkenes catalysed by MTO in trifluoroethanol^a

Alkene	t/h	Yield (%)
Hex-1-ene	6	95
	21	>99
Hept-1-ene	21	>99
Oct-1-ene	21	>99
Non-1-ene	21	>99
Dec-1-ene	21	97
Vinylcyclohexane	21	>99
Styrene	2	82 ^b
3-Phenylpropene	21	97
4-Phenylbut-1-ene	21	>99

^a Conditions: 10 mmol alkene, 1 mmol Bu_2O (internal standard), 0.010 mmol MeReO_3 (0.1 mol%), 0.5 mmol pyrazole, 20 mmol 60% H_2O_2 and 5 ml trifluoroethanol. Stirring at room temperature, analysis by GC.

^b Phenylethane-1,2-diol and benzaldehyde were also detected.

Table 2 Epoxidation of internal alkenes catalysed by MTO in trifluoroethanol^a

Alkene	t/h	Yield (%)
Cyclohexene	0.5	>99
Cycloheptene	1	>99
Cyclooctene	1	>99
1-Methylcyclohexene	0.5	>99
Methylenecyclohexane	1	99
Indene	1	65 ^b
2-Methylhept-1-ene	1.5	98
2-Methylhept-2-ene	1	99

^a Conditions: 1 mmol Bu₂O (internal standard), 0.010 mmol MeReO₃ (0.1 mol%), 1 mmol pyrazole and 20 mmol 60% H₂O₂ were dissolved in 5 ml trifluoroethanol. The stirred mixture was cooled in an ice bath to ca. 5 °C. The alkene (10 mmol) was then added dropwise in 20–30 min. The mixture was warmed to room temperature and analysed by GC. ^b Several hydrolysis products were also detected.

with 0.1 mol% of catalyst. The epoxide was formed with high selectivity and no noticeable by-products were observed. The only notable exception was styrene. Its very sensitive epoxide was partly decomposed to phenylethane-1,2-diol and benzaldehyde. The yield, however, is comparable to the best results claimed by Sharpless and co-workers.⁶ These high turnovers obtained for terminal alkenes are unprecedented and can only be approached by the recently improved manganese triazonane catalyst.⁹

The high turnovers could also be obtained in the oxidation of the more reactive internal alkenes. However, the reaction was in several cases too fast, resulting in the decomposition of the catalyst and incomplete conversion of the alkene. When appropriate cooling was applied, no catalyst decomposition was observed. A better procedure was to add the substrate slowly (ca. 20 to 30 min) to the ice-cooled reaction mixture. In most cases the reaction was complete within minutes after the addition of the last portion of alkene. The presence of the active catalyst, even after 1000 turnovers, was indicated by the intense yellow colour of the peroxo complex. The results for some internal alkenes are shown in Table 2. Most epoxides give >99% yield of epoxide, except indene. Indene oxide is known to be very sensitive towards hydrolysis. The homogeneous reaction mixture with water present in the same phase as the epoxide results in decomposition of the product. The two-phase system with CH₂Cl₂ generally gives higher yields, because the water and epoxide are present in separate phases. This behaviour is known for other catalytic systems as well.¹⁰ Most other epoxides, however, are stable enough to resist hydrolysis in a monophasic system.

The catalyst is still active after 1000 turnovers, and 2500 turnovers could be obtained by slow addition of alkene to the reaction mixture. At a substrate to catalyst ratio of 2000 complete conversion was reached within 1 h with cyclohexene.

At a substrate to catalyst ratio of 3000 the catalyst decomposed and only 90% conversion could be reached. These high turnovers require very careful addition of the alkene. A slightly faster addition of the alkene than the optimum addition rate causes the reaction mixture to warm up, resulting in complete loss of catalytic activity.

One disadvantage of the present catalytic system is the high polarity of the reaction medium. Very apolar alkenes (C₁₂ or higher alkenes and stilbenes) do not dissolve in the reaction medium, and are therefore not epoxidised. In other cases (the experiments of Table 1 and 2) the alkene does not dissolve completely at the beginning of the reaction. During the course of the reaction the medium becomes homogeneous due to the formation of polar, soluble epoxide. The time required for a homogeneous reaction mixture depends on the polarity of the alkene and ranges from 1 h for hex-1-ene to 6 h for dec-1-ene. The more reactive internal alkenes give a homogeneous reaction mixture within minutes after the addition.

In summary, the use of MTO–pyrazole in trifluoroethanol allows for the highly selective epoxidation of a variety of olefins with 30–60% aqueous H₂O₂ at low (0.1 mol%) catalyst loading. The methodology should have wide applicability in organic synthesis.

Notes and references

- 1 G. Strukul and R.A. Michelin, *J. Chem. Soc., Chem. Commun.*, 1984, 1538; C. Venturello and R. D'Aloisio, *J. Org. Chem.*, 1988, **53**, 1553; Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida and M. Ogawa, *J. Org. Chem.*, 1988, **53**, 3587; K. Sato, M. Aoki, M. Ogawa, T. Hashimoto and R. Noyori, *J. Org. Chem.*, 1996, **61**, 8310; T. Kamiyama, M. Inoue, H. Kashiwagi and S. Enomoto, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1559; P. L. Anelli, S. Banfi, F. Montanari and S. Quici, *J. Chem. Soc., Chem. Commun.*, 1989, 779; D. de Vos and T. Bein, *Chem. Commun.*, 1996, 917; M. G. Clerici and P. Ingallina, *J. Catal.*, 1993, **140**, 71.
- 2 M. Rüsche, gen. Klaas, Thesis RWTH Aachen, 1993.
- 3 W. A. Herrmann, R. W. Fischer and D. W. Marz, *Angew. Chem.*, 1991, **103**, 1706; W. A. Herrmann, D. W. Marz, W. Wagner, J. G. Kuchler, G. Weichselbaumer and R. W. Fischer, *Ger. Pat.*, 3902357, 1989 to Hoechst AG.
- 4 W. A. Herrmann, R. W. Fischer, M. U. Rauch and W. Scherer, *J. Mol. Catal.*, 1994, **86**, 221.
- 5 J. Rudolph, K. L. Reddy, J. P. Chiang and K. B. Sharpless, *J. Am. Chem. Soc.*, 1997, **119**, 6189.
- 6 C. Copéret, H. Adolfsson and K. B. Sharpless, *Chem. Commun.*, 1997, 1565.
- 7 W. A. Herrmann, R. M. Kratzer, H. Ding, W. R. Thiel and H. Glas, *J. Organomet. Chem.*, 1998, **555**, 293.
- 8 M. C. A. van Vliet, I. W. C. E. Arends and R.A. Sheldon, manuscript in preparation.
- 9 D. E. de Vos, B. F. Sels, M. Reynaers, Y. V. Subba Rao and P. Jacobs, *Tetrahedron Lett.*, 1998, **39**, 3221.
- 10 K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, D. Panyella and R. Noyori, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 905.

Communication 9/02133G