

A Very Efficient Alkene Epoxidation by Magnesium Monoperoxyphthalate Catalysed by Manganese Porphyrins

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Mn-porphyrins catalyse the epoxidation of various alkenes by magnesium monoperoxyphthalate: with 0.125–1% of tetra-2,6-dichlorophenylporphinatomanganese(III) acetate as a catalyst, alkene conversion is nearly complete within 0.5–5 minutes at 0 °C and good epoxide yields (60–93%) are obtained.

Recently much attention has been devoted to metalloporphyrin-catalysed oxygenations of hydrocarbons in order to develop new useful synthetic methods and to mimic the activity of the cytochrome P-450 enzymes.¹ Many oxidants have been evaluated as oxygen donors in these catalytic reactions (*e.g.* iodosylarenes, sodium hypochlorite, molecular oxygen, alkylhydroperoxides, hydrogen peroxide, amine *N*-oxides, potassium hydrogen persulphate)^{1a} but, surprisingly, organic peroxy acids have received little attention.²

We have now found that a stable, cheap, recently developed water-soluble peracid derivative, the magnesium monoperoxyphthalate,³ is a very efficient reagent for the epoxidation of alkenes under phase-transfer conditions and in the presence of Fe- or Mn-porphyrins as catalysts. The best results were obtained with 5,10,15,20-tetra-2,6-dichlorophenylporphinatomanganese(III) acetate (TDCPP-Mn), a complex known to be remarkably stable towards oxidative degradation.⁴ TDCPP-Fe also catalyses alkene epoxidation, but it is less efficient than the manganese complex. Small yields of epoxide, if any, are obtained when the reactions are repeated in the absence of the metal porphinate.

With magnesium monoperoxyphthalate, like with other oxygen donors,^{1a} the addition of a heterocyclic nitrogen base (pyridine or 4-methylpyridine) remarkably improves the epoxidation rate, although it is not a necessary condition for the reaction. In the presence of the base, even electron-poor alkenes, such as isobutyl-3-butenate, are efficiently epoxidised under very mild conditions. In a typical experiment the manganese complex (5 µmol), 4-methylpyridine (0.2 mmol), benzyltrimethylammonium chloride (10 µmol), and the alkene (0.5–4 mmol, see Table 1) are dissolved in 2.5 ml of dichloromethane and the resulting solution is cooled to 0 °C. Then magnesium monoperoxyphthalate (filtered 20% aqueous solution, 2 mol per mol of alkene) is added and the reaction is initiated by vigorous stirring. After the required time the aqueous and the organic layers are separated. The latter is analysed by g.l.c. with *n*-dodecane or *n*-octadecane as an internal standard. Some significant results are reported in Table 1. Turnover rates as high as 1600 (epoxide/catalyst)/min for styrene epoxidation are obtained, thus indicating that this catalytic system is considerably more efficient than most of those previously described. To the best of our knowledge only

Table 1. Epoxidation of alkenes by magnesium monoperoxyphthalate catalysed by Mn- or Fe-porphinates.^a

Alkene	Porphinate	Nitrogen Base	[Alkene]/ [porphinate]	Time/ min	Alkene conversion/%	Epoxide yield ^b /%
Styrene	None	4-Methylpyridine	^c	0.5	^d	1
"	TPP-Mn ^e	"	200	2	67	38
"	TDCPP-Fe	"	800	0.5	37	12
"	TDCPP-Mn	"	800	0.5	100	90
Dodec-1-ene	"	"	400	4	96	77
Isobutyl-3-butenate	"	"	100	2	92	60
Cyclo-octene	"	"	800	3	100	93
"	"	Pyridine	800	3	100	92
"	"	None	800	3	65	61

^a Conditions as described in the text. ^b Yields (based on starting alkene) were determined by g.l.c. using an internal standard. ^c Styrene: 4 mmol. ^d Not determined. ^e TPP-Mn: 5,10,15,20-tetraphenylporphinatomanganese(III) chloride.

the use of iodosylpentafluorobenzene, a sophisticated and dangerous⁵ oxygen donor, allows higher reaction rates, up to 300 turnovers per sec in the epoxidation of norbornene.⁶

In the case of reactive alkenes (*e.g.* *cis*-cyclo-octene), 50 000 moles of substrate are converted by one mole of catalyst (room temp., overnight, pH of the aqueous phase adjusted to 6.5 to prevent the epoxide hydrolysis; epoxide yield 93%). With less reactive substrates, the competitive oxidation of the porphyrin itself becomes important and when isobutyl-3-butenolate is used as the substrate the catalyst is completely destroyed after 100 turnovers.

It is worth noting that, in the absence of a reactive substrate, TDCPP-Mn shows a considerable 'catalase activity' and extensive decomposition of the peroxyphthalate occurs.

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References

- 1 (a) B. Meunier, *Bull. Soc. Chim. Fr.*, 1986, 578; (b) P. R. Ortiz de Montellano, 'Cytochrome P-450, Structure, Mechanism and Biochemistry,' Plenum Press, New York and London, 1986; (c) D. Mansuy, *Pure Appl. Chem.*, 1987, **59**, 759.
- 2 J. T. Groves, R. C. Haushalter, M. Nakamura, T. E. Nemo, and B. J. Evans, *J. Am. Chem. Soc.*, 1981, **103**, 2884; J. T. Groves, Y. Watanabe, and T. J. McMurry, *ibid.*, 1983, **105**, 4489; J. R. Lindsay Smith, M. W. Nee, J. B. Noar, and T. C. Bruice, *J. Chem. Soc., Perkin Trans. 2*, 1984, 255; T. G. Traylor, W. A. Lee, and D. V. Stynes, *J. Am. Chem. Soc.*, 1984, **106**, 755; W. A. Lee, L. Yuan, and T. C. Bruice, *ibid.*, 1988, **110**, 4277.
- 3 P. Brougham, M. S. Cooper, D. A. Cummerston, H. Heaney, and N. Thompson, *Synthesis*, 1987, 1015.
- 4 S. Banfi, F. Montanari, and S. Quici, *J. Org. Chem.*, 1988, **53**, 2863 and references therein.
- 5 J. P. Collman, *Chem. Eng. News*, 1985, **63**, 2.
- 6 T. G. Traylor, J. C. Marsters, Jr., T. Nakano, and B. E. Dunlap, *J. Am. Chem. Soc.*, 1985, **107**, 5537.