Regioselective Epoxidations of Dienes with Manganese(III) Porphyrin Catalysts

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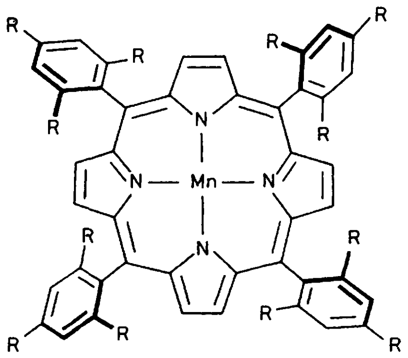
A series of sterically hindered manganese porphyrins are shown to be shape-selective catalysts for the epoxidation of a variety of dienes; product ratio differences for conjugated *vs.* non-conjugated dienes indicate the existence of at least two competing epoxidation pathways.

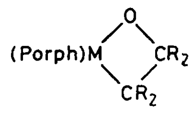
The flexibility of epoxides as useful intermediates in organic synthesis[1] has led to diverse efforts to devise selective catalytic epoxidation systems. For example, the epoxidation of allylic enols over isolated double bonds and the enantioselective epoxidation of allylic alcohols have been reported by Sheng[2] and Sharpless,[3] respectively. However, when dienes are epoxidized by peroxyacids or by hydroperoxides and $Mo(CO)_6$, the most electron-rich double bond (*i.e.*, that with the most alkyl substituents) is selectively attacked.[2] Efforts to use bulky molybdenum catalysts for selective epoxidation of more accessible, but less nucleophilic, double bonds have had only limited success.[4]



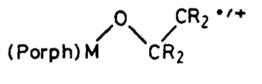
R = H, Mn(TPP)
R = OMe, Mn(TTMPP)
R = Ph, Mn(TTPPP)

We report here that an extremely hindered bis-pocket porphyrin complex, 5,10,15,20-tetrakis(2,4,6-triphenylphenyl)porphyrinato(acetato)manganese(III) [Mn(TTPPP)(OAc)] is an efficient shape-selective catalyst for the sterically most accessible double bonds in unfunctionalized dienes.

Manganese porphyrins have been used as effective catalysts for the epoxidation of alkenes with various oxidants,[5—7] in analogy to similar chemistry by cytochrome P-450. Collman and Meunier[5] have used manganese porphyrin imidazole



(A)



(B)

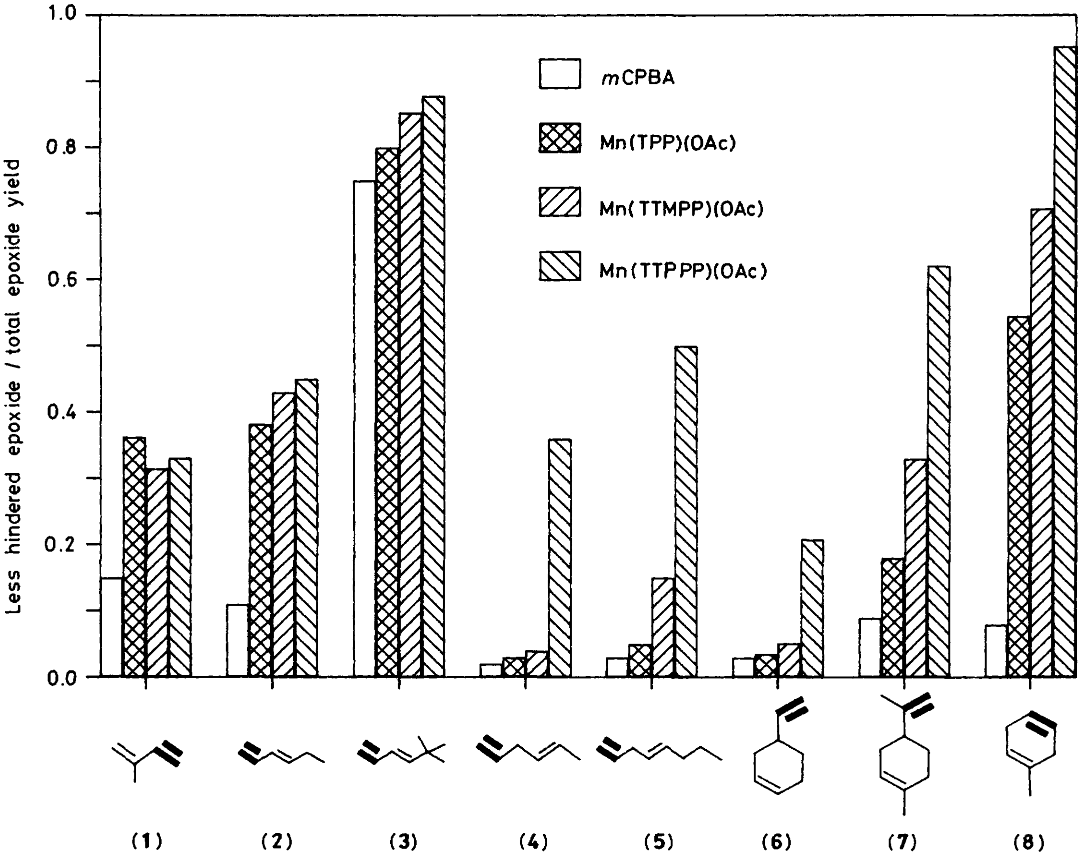


Figure 1. Ratio of less hindered epoxide to total epoxide produced. The less hindered double bond is highlighted in the drawings of the diene substrates. All manganese porphyrin reactions were run using the same conditions: 1 mmol of diene substrate, 0.07 mmol of NaOCl (commercial bleach), 0.5 µmol of manganese porphyrin, and 10 µmol of 4'-(imidazol-1-yl)acetophenone in 0.5 ml of methylene chloride, 15 min at 300 K. Products were analysed using capillary g.c. and g.c.–mass spectrometry. Yields of epoxides were 60—80% based on NaOCl for all reactions; only small amounts of allylic oxidation products were detected.

complexes for epoxidation with aqueous hypochlorite, and proposed a metallaoxetane intermediate (A) in these oxidations, similar to that proposed by Sharpless[8] for perchromate epoxidations of alkenes. Consistent with this mechanism, modest shape selectivity is observed for *cis*- *vs*. *trans*-alkenes with slightly sterically hindered manganese porphyrin catalysts. Alternatively, an electron transfer mechanism has been proposed by Lindsay Smith,[11] Mansuy,[12] and Traylor[13] for epoxidation by iron porphyrin catalysts, involving a ring-opened intermediate (B).

A series of non-conjugated dienes of varying shapes and sizes were epoxidized using aqueous NaOCl (bleach) in the presence of imidazole and three different manganese porphyrins with differing degrees of steric constraint. In all cases, Mn(TTPPP)(OAc) shows enhanced selectivity for epoxidation of the most exposed double bond of the substrate (Figure 1). With non-conjugated straight-chain dienes (*e.g.*, *trans*-hexa-1,4-diene (**4**) or *trans*-octa-1,4-diene (**5**), Mn(TTPPP)(OAc) shows a remarkable preference for epoxidation at the terminal position, when compared to the unhindered Mn(TPP)(OAc) (TPP = tetraphenylporphyrinato) or even the modestly hindered Mn(TTMPP)(OAc) [TTMPP = tetrakis(2,4,6-trimethoxyphenyl)porphyrinato]. As expected, this selectivity for terminal epoxidation increases as the steric bulk of the diene increases, similar to the trend which we have observed in the hydroxylation of n-alkanes by these same catalysts.[10] The shape selectivity originates from the steric demands of the metalloporphyrins' superstructures. In keeping with this, the ratio of enhancement for terminal epoxidation in going from C_6 to C_8 is very similar to that observed for hydroxylation.

Limonene (**7**) and its structural analogue 4-vinylcyclohexene (**6**) are useful chiral starting materials for many organic syntheses. However, in all previous cases, epoxidation of these molecules gave exclusively ring epoxidation rather than external epoxidation. This is still the case with the unhindered Mn(TPP)(OAc) and the modestly hindered Mn(TTMPP)(OAc). The extremely hindered Mn(TTPPP)(OAc), however, enhances the epoxidation of the external double bond of 4-vinylcyclohexene (**6**), and for the more sterically demanding limonene (**7**), external epoxide is the major product.

Extremely high selectivity is observed in the epoxidation of 1-methylcyclohexa-1,4-diene (**8**) for the sterically less hindered double bond. This is consistent with a metallaoxetane intermediate. Even the unencumbered Mn(TPP)(OAc) gives a large enhancement in selectivity relative to uncatalysed epoxidation with *m*-chloroperoxybenzoic acid, which involves the sterically less sensitive 3-membered intermediate [Mn(TPP)(OAc) shows modest enhancements compared to *m*-chloroperoxybenzoic acid for all substrates examined]. Mn(TTPPP)(OAc), with its very hindered pockets, gives almost *exclusive* epoxidation of the disubstituted double bond.

When conjugated dienes are epoxidized [*e.g.*, isoprene (**1**), *trans*-hexa-1,3-diene (**2**), or *trans*-5,5-dimethylhexa-1,3-diene (**3**)] selectivity enhancements for terminal epoxidation are observed in all cases, except the small isoprene molecule. The magnitudes of the enhancements, however, are very small when compared to the non-conjugated systems (Figure 1), indicating an intermediate of quite different steric constraints. The 1,3-dienes, which are more electron rich, may be epoxidized *via* an electron transfer mechanism similar to those suggested for iron porphyrins,[11—13] rather than *via* a more sterically demanding mechanism. These results clearly eliminate the formation of either metallaoxetane or (from a 4 + 2 addition) metallaoxacyclohexene intermediates in the epoxidation of 1,3-dienes.

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