Metalloporphyrin-catalysed Epoxidation of Terminal Aliphatic Olefins with Hypochlorite Salts or Potassium Hydrogen Persulphate

Bertha De Poorter and Bernard Meunier*
Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31400 Toulouse, France

Substitution of tetraphenylporphyrinatomanganese(III) complexes on the peripheral phenyl groups makes these compounds suitable as catalysts for the epoxidation of terminal olefins with mono-oxygen donors such as sodium or lithium hypochlorite and potassium hydrogen peroxomonosulphate in a biphasic system.

During the last five years, several systems have been studied which can be considered as models for the enzymic monooxygenation of hydrocarbons by cytochrome P-450; in these model systems, a synthetic metalloporphyrin is used to catalyse the transfer of one oxygen atom to the hydrocarbon substrate, either from a single-oxygen donor (*e.g.* PhIO,[1] NaOCl,[2] *p*-cyano-*N*,*N*-dimethylaniline *N*-oxide,[3] $Bu_4{}^nIO_4$,[4] or ROOH[5]) or from a combination of molecular oxygen and a reducing agent (*e.g.* H_2,[6] ascorbate,[7] tetrahydridoborate[8]).[†] Although di-, tri-, and tetra-substituted aliphatic olefins can be epoxidised in fair yields with some of these systems,[1a—d,2b—d,4,6] attempted epoxidation of aliphatic terminal olefins has been rather unsuccessful hitherto,[1b,1c,2c,2d] the highest turnover number described in the literature being four cycles.[1b] As the epoxidation of the alkene and the oxidative decomposition of the catalyst are competing processes in these systems, the catalyst is destroyed before these relatively unreactive olefins can be epoxidised successfully. Therefore, we searched for catalysts that are stabilised against decomposition and studied their activity in terminal olefin epoxidation. Here we report that terminal olefins can be epoxidised with hypochlorite in high yields (60—80%) when substituents are introduced on the peripheral phenyl groups of the porphyrin ligand of the catalyst. We further report our results with other mono-oxygen donors.

Results and Discussion

Epoxidation of Aliphatic Terminal Olefins with Sodium and Lithium Hypochlorite, catalysed by Substituted Tetraphenylporphyrinatomanganese(III) *Complexes.*—In a previous paper,[2d] various di- and tri-substituted aliphatic olefins and styrene were shown to be epoxidised in good yields with the biphasic NaOCl–Mn(tpp)OAc system. However this system was not suitable for the epoxidation of terminal aliphatic olefins; *e.g.* oct-1-ene was 5% converted (yielding 1% of epoxide) when the catalyst was destroyed. The mechanism was shown to be compatible with the transfer of an electrophilic oxygen atom in a *syn*-addition, and possible intermediate high-valent manganese complexes were discussed.

In a preliminary communication[10] we described how the substitution of the peripheral phenyl groups of the tetraphenylporphyrin ligand considerably enhances the conversion of oct-1-ene and the yield of the corresponding epoxide (Table 1). Functionalised olefins, such as 5-bromopent-1-ene and pent-4-enyl acetate, were also epoxidised, in 40—70% yield.

During subsequent work, we noticed that the origin of the commercially available hypochlorite solution influenced the reaction course, especially the rate of epoxidation. This appeared to be due in part to a different content of sodium hydroxide.[‡] As the epoxidations mentioned in Table 1 were not all performed with the same batch of commercial sodium hypochlorite (Prolabo), a too strict comparison between the activities of different catalysts must be avoided. In order to provide a better scale of catalytic activity for these substituted-phenylporphyrinato ligands, we performed the epoxidation of oct-1-ene with lithium hypochlorite solutions containing known hydroxide concentrations (Tables 2 and 3). Although *para*-substitution can increase the conversion of oct-1-ene up to 70%, the epoxide yield remains low (Tables 1 and 2); the results obtained with Mn(tF$_5$pp)Cl, Mn(*o*Fpp)Cl, Mn(*o*Clpp)Cl, Mn(tmp)Cl, and Mn(TCl$_2$pp)Cl demonstrate that *ortho*-substitution is imperative for an increase in selectivity. The enhanced activity of M(tF$_5$pp)Cl (M = Fe or Mn) as compared with the tpp-analogues as catalysts in the oxidation of cyclohexene, cyclohexane, and anisole with iodosylbenzene has been mentioned before by Chang *et al.*,[1d] who ascribed this to an enhanced stability and electrophilicity of the complex. We determined the stability of different catalysts by measuring the intensity of the Soret absorption at the end of the reaction of oct-1-ene with 1 equiv. of LiOCl (Table 4). Although *para*-substitution with a trifluoromethyl group considerably stabilises the complex [53% of the complex left, as compared with only 2% in the case of Mn(tpp)OAc], allowing a fair conversion of oct-1-ene, the more stable catalysts are those with *ortho*-substituents (70—80% left). As these substituents may be halogens or methyl groups, these results seem to indicate that in the case of the epoxidation of oct-1-ene, steric effects play an important role in the reaction course, by increasing the stability of the catalyst (and as a consequence, the conversion of oct-1-ene) as well as by improving the selectivity. We checked the stability of 1,2-epoxyoctane under the reaction conditions (replacing oct-1-ene by hex-1-ene) in the presence of Mn(tF$_5$pp)Cl, Mn(*o*Clpp)Cl, and Mn(*p*Trifpp)Cl; in these three cases, about 90% of 1,2-epoxyoctane was recovered, demonstrating that the increase of selectivity with *ortho*-substitution is not due to a decreased reactivity of the epoxide formed, but to steric interactions with the olefin during oxygen transfer from metal to substrate.

Comparison of Tables 2 and 3 shows that the selectivity is slightly influenced by increasing the hydroxide concentration from 0.03 to 0.13 mol dm^{-3} (in both cases, [OCl$^-$] is *ca.* 0.30 mol dm^{-3}). However, the dependence of epoxidation rate on hydroxide concentration is not the same for different catalysts. Although the Mn(tmp)Cl- and Mn(*o*Clpp)Cl-catalysed reactions are rather insensitive to this change,[§] Mn (*o*Fpp)Cl- and

---

[†] For a recent review of homogeneous catalytic oxidations, see reference 9.

[‡] Hydroxide concentration in different commercially available solutions varied from *ca.* 0.03 (Prolabo) to 0.33 mol dm^{-3} (Janssen).

[§] However, other factors seem also to interfere: as the Mn(*o*Clpp)Cl-catalysed epoxidation, which is insensitive to OH$^-$ content, was much slower when commercial sodium hypochlorite was used (Table 1).

Table 1. Epoxidation of terminal aliphatic olefins with NaOCl

Olefin	Catalyst[a]	% Catalyst *vs.* olefin	Conversion of olefin (%)[b]	Yield of epoxide (%)[b]	Selectivity (%)[b]	Reaction time (h)
Oct-1-ene	Mn(tpp)OAc	0.6		1[d]		4
	Mn(*p*Fpp)Cl	0.8	43	21	49	3.75
	Mn(*p*Trifpp)Cl	0.7	71	34	48	3
	Mn(*o*Fpp)Cl	0.8	88	59	67	1.75
	Mn(*o*Clpp)Cl	0.9	>99	89	89	5.25
	Mn(tF$_5$pp)Cl	0.7	>95	68	*ca.* 68	3
	Mn(tCl$_2$pp)Cl[c]		89	81	91	8.25
Vinylcyclohexene	Mn(tF$_5$pp)Cl	0.6		50		4
Propene	Mn(tF$_5$pp)Cl	0.6	100	*ca.* 51	*ca.* 51	3
5-Bromopent-1-ene	Mn(tF$_5$pp)Cl	0.6	94	69	73	2.5
	Mn(*o*Fpp)Cl	0.7	98	51	52	3.25
Pent-4-enyl acetate	Mn(tF$_5$pp)Cl	0.6	100	41	41	3.25

[a] tpp = *meso*-tetraphenylporphyrinato dianion; in the other complexes the phenyl groups are replaced by C_6F_5 (tF$_5$pp), *p*-FC_6H_4 (*p*Fpp), *p*-$CF_3C_6H_4$ (*p*Trifpp), *o*-FC_6H_4 (*o*Fpp), *o*-ClC_6H_4 (*o*Clpp), and 2,6-$Cl_2C_6H_3$ (tCl$_2$pp). [b] Conversion and yield determined by g.l.c. analysis. As defined by Sheldon and Kochi, [23] the conversion is the amont of consumed reactant, *i.e.* olefin; the yield is the amount of product formed *vs.* the initial amount of reactant; the selectivity is the yield divided by the conversion. [c] Impure sample of catalyst. [d] Data from refs. 2*c* and 2*d*.

Table 2. Epoxidation of oct-1-ene with LiOCl ([OH$^-$] = 0.03 mol dm^{-3}).

Catalyst[a]	% Cat. *vs.* oct-1-ene	Conversion of oct-1-ene (%)[b]	Yield of epoxide (%)[b]	Selectivity (%)[b]	Reaction time (h)[c]	Equiv. of LiOCl
Mn(tF$_5$pp)Cl	0.7	100	56	56[f]	3	2.2
	0.7	72	52	72	3	1[e]
Mn(*o*Fpp)Cl	0.8	94	62	66	1	2.2
	0.8	66	45	68	1	1[e]
Mn(*o*Clpp)Cl	0.9	100	80	80	1.5	2.2
	0.8	73	60	82	1.5	1[e]
Mn(tmp)Cl	0.7	95	73	77	5	2.2
	0.7	71	53	75	24[d]	1[e]
Mn(*p*Trifpp)Cl	0.7	73	30	41	2	2.2
	0.8	57	27	47	3.5	1[e]

[a] See Table 1; tmp = *meso*-tetramesitylporphyrinato dianion. [b] See Table 1. [c] The reaction was monitored by analysing 1 μl samples by g.l.c.; time intervals were 1/4, 1/2, or 1 h, depending on the reaction rate. Work-up was carried out when more than 90% of oct-1-ene was converted, or when the epoxide:octene ratio did not change any more. [d] As the reaction was not finished after 7 h, the mixture was kept overnight. [e] The conversion of LiOCl was complete. [f] With this catalyst, the selectivity drops when the reaction is run to complete conversion of oct-1-ene.

Table 3. Epoxidation of oct-1-ene with LiOCl ([OH$^-$] = 0.13 mol dm^{-3}; 2.3 equiv. LiOCl *vs.* oct-1-ene)

Catalyst[a]	% Cat. *vs.* oct-1-ene	Conversion of oct-1-ene (%)[b]	Yield of epoxide (%)[b]	Selectivity (%)[b]	Reaction time (h)[c]
Mn(tF$_5$pp)Cl	0.7	50	34	68	6
Mn(*o*Fpp)Cl	0.8	93	58	62	2
Mn(*o*Clpp)Cl	0.9	100	73	73	2
Mn(tmp)Cl	0.7	92	71	77	4.5

[a] See Table 2. [b] See Table 1. [c] See Table 2; in the case of Mn(tF$_5$pp)Cl, the reaction was not finished after 6 h.

Table 4. Epoxidation of oct-1-ene with 1 equiv. of LiOCl ([OH$^-$] = 0.03 mol dm^{-3}): determination of catalyst stability

Catalyst[a]	Conversion of oct-1-ene (%)[b]	Yield of epoxide (%)[b]	Selectivity (%)[b]	Conversion of LiOCl	% of catalyst after reaction
Mn(tF$_5$pp)Cl	75	50	67	>99	80
Mn(*o*Fpp)Cl	68	48	71	>99	82
Mn(*o*Clpp)Cl	70	63	90	>99	72
Mn(tmp)Cl	74	58	78	>99	69
Mn(*p*Trifpp)Cl	65	28	43	>99	53
Mn(tpp)OAc	24	6	25	40	*ca.* 2

[a] See Table 2. [b] See Table 1.

Table 5. Epoxidation of olefins with potassium hydrogen persulphate

Olefin	Catalyst[a]	% Catalyst *vs.* olefin	Conversion of olefin (%)[a]	Yield of epoxide (%)[a]	Selectivity (%)[a]	Reaction time (h)
Cyclohexene	Mn(tpp)OAc	1.5	83	65	79	1
	Mn(tF$_5$pp)Cl	1.3	100	100	100	0.5
	Fe(tpp)Cl	1.8	58	18	31	2
	Cr(tpp)Cl	1.8	75	10	13	2
	Mn(*p*Fpp)Cl	1.6	90	44	49	1
	—		28	13	46	1
Oct-1-ene	Mn(tpp)OAc	1.7		5		3
	Mn(tF$_5$pp)Cl	1.4	100	61	61	1.15
	Mn(*o*Fpp)Cl	1.6	36	11	31	0.5
	Mn(*o*Clpp)Cl	1.7	74	38	51	2.25
	Mn(*p*Fpp)Cl	1.3	50	<3	<6	1.5
	Mn(*p*Trifpp)Cl	1.3	37	<6	<16	0.25
5-Bromopent-1-ene	Mn(tF$_5$pp)Cl	1.0	96	45	47	6.5
Pent-4-enyl acetate	Mn(tF$_5$pp)Cl	0.9	97	56	58	4
1-Methylcyclohexene	Mn(tpp)OAc	1.1		70		1
Styrene	Mn(tpp)OAc	1.3	78	32	41	1
	Mn(tF$_5$pp)Cl	1.0	100	75	75	0.5

[a] See Table 1.

Mn(tF$_5$pp)Cl-catalysed epoxidations appear to slow down considerably when the hydroxide concentration increases, especially the latter reaction, where after 6 h only 50% conversion was observed instead of complete conversion after 3 h. This seems to point to the formation of a less active complex, stabilised by the electronegative fluorine substituent(s) (hydroxy complex? μ-oxo dimer?).

While our work was in progress, two papers[11,12] were published which also stressed the influence of intermolecular interactions on the catalytic activity of porphyrinate complexes. By anchoring Mn(tpp)OAc to a rigid polymer, Van der Made *et al.*[11] succeeded in increasing the rate of cyclohexene epoxidation with NaOCl; they explained this in terms of the prevention of formation of a less active μ-oxo dimer. Traylor *et al.*[12] demonstrated the stability of *meso*-tetrakis-(2,6-dichlorophenyl)porphyrinatoiron(III) chloride and *meso*-tetrakis(pentachlorophenyl)porphyrinatoiron(III) chloride in the Fe(por)Cl–C_6F_5IO system (por = general porphyrinato), and the very high turnover obtained for norbornene epoxidation.

Thus it seems that to increase the activity of the catalyst one should avoid too close an approach of two catalyst molecules; however, the selectivity of terminal olefin epoxidation appears to depend largely on steric interactions between the active catalytic species and the olefin.

*Influence of Fluoride on the Epoxidation Rate of Oct-*1-*ene with Calcium Hypochlorite.*—Under normal conditions, *i.e.* Mn(por)X–(OCl^- + pyridine) (as described for LiOCl in the Experimental section), a 67% yield of 1,2-epoxyoctane was obtained after *ca.* 1.5 h, when calcium hypochlorite was used as the oxygen donor and Mn(tF$_5$pp)Cl as catalyst (conversion 94%, selectivity 71%). Unexpectedly, we noticed that the addition of sodium fluoride to this system caused a pronounced rate enhancement. Indeed, by adding 1 equiv. of sodium fluoride *vs.* hypochlorite, we obtained a 57% yield of epoxide after only 10 min, which corresponds to a turnover rate of *ca.* 560 cycles per hour[*] (conversion 82%, selectivity 70%). That the fluoride anions do not completely take over the role of pyridine as the co-ordinating species[†] is shown when this turnover drops to *ca.* 160 cycles per hour (16% yield after 10 min) in the absence of pyridine, which is still a remarkable value for a terminal olefin. Unfortunately, in the presence of fluoride, these reactions are accompanied by the formation of intractable emulsions. Because the addition of sodium fluoride has no significant effect in the cases of NaOCl and LiOCl, and because of the low solubility of CaF_2 and the observation of emulsions, we believe that this rate enhancement is a purely physical process (influence on phase transfer?), the nature of which goes beyond the scope of this work.

Epoxidation with Other Mono-oxygen Donors.—In order to extend the scope of the reaction, we studied other easily available reagents as potential oxygen donors, such as potassium hydrogen peroxomonosulphate ($KHSO_5$) and sodium perborate.

Potassium hydrogen persulphate has been used before to oxidise sulphides to sulphones,[13] to epoxidise olefins in the presence of acetone,[14] and to cleave the *ortho*-benzoquinone ring.[15]

The results we obtained in the cyclohexene epoxidation show that iron or chromium porphyrinates are not suitable as epoxidation catalysts (Table 5); in our laboratory this distinctive behaviour of manganese porphyrinates as compared with other complexes has already been observed for epoxidation with NaOCl.[2b,d] The fluorinated complex Mn(tF$_5$pp)Cl is particularly active; after 0.5 h the conversion of cyclohexene is complete, and a quantitative yield of the epoxide is obtained. Moreover, this complex is an excellent catalyst for the epoxidation of oct-1-ene, and to a lesser extent, of the functionalised terminal olefins 5-bromopent-1-ene and pent-4-enyl acetate. The Mn(tpp)OAc- and Mn(tF$_5$pp)Cl-catalysed

---

[*] This is not the initial rate of epoxide formation, but is based on the epoxide yield (57%) after 10 min (catalyst: 0.61% *vs.* oct-1-ene).

[†] For a discussion of the role of pyridine in the Mn(por)X–OCl^- system, see references 2*b*—*d*.

Table 6. Influence of pyridine on epoxidation with potassium hydrogen persulphate[a]

Olefin	Catalyst[b]	% catalyst *vs.* olefin	Conversion of olefin (%)[b]	Yield of epoxide (%)[b]	Selectivity (%)[b]	Reaction time (h)
Oct-1-ene	Mn(tpp)OAc	1.7	60	17	28	0.5
	Mn(tF_5pp)Cl	1.4	93	81	87	1.25
	Mn(*o*Fpp)Cl	1.5	100	67	67	0.75
	Mn(*o*Clpp)Cl	1.7	98	73	74	1.15
Styrene	Mn(tpp)OAc	1.3	100	59	59	1
	Mn(tF_5pp)Cl	1.0	96	78	81	0.5

[a] Pyridine–oct-1-ene 2.0:1; pyridine–styrene 1.4:1. [b] See Table 1.

epoxidations of cyclohexene, as well as the Mn(tF_5pp)Cl-catalysed epoxidation of oct-1-ene, are faster when $KHSO_5$ is used instead of NaOCl (*cf.* reference 2*d*). As we had noticed the influence of hydroxide concentration on the rate of oct-1-ene epoxidation with LiOCl–Mn(tF_5pp)Cl, this could explain the higher rate obtained with the persulphate system, which has a much lower pH (8 instead of 12—13). Unfortunately however, this rate enhancement is accompanied by a still faster decomposition of the catalyst: *e.g.* the reaction mixture oct-1-ene–Mn(*o*Fpp)Cl–$KHSO_5$ is bleached in about 15 min, resulting in a low yield (11%) of 1,2-epoxyoctane.

It was previously observed in this laboratory[2c,d] that addition of pyridine to the Mn(tpp)OAc–NaOCl system caused an increase in both selectivity and epoxidation rate, which was attributed to pyridine co-ordination on the manganese complex. A comparison of Tables 5 and 6 shows that pyridine has an analogous effect on epoxidation with $KHSO_5$. This improvement of the reaction course is accompanied by an increased stability of the catalyst, resulting in fair yields with Mn(*o*Fpp)Cl and Mn(*o*Clpp)Cl. Under these conditions, a selectivity as high as 87% (at 93% conversion) is obtained for the epoxidation of oct-1-ene catalysed by Mn(tF_5pp)Cl, corresponding to a turnover of 46 cycles per hour.

Unexpectedly, even in the presence of pyridine, the combination Mn(tpp)OAc–$KHSO_5$ is less efficient than Mn(tpp)OAc–NaOCl for the epoxidation of styrene; with the latter system, this olefin is smoothly oxidised (80% epoxide in 30 min[2c,d]) and reacts faster than other (even di- and tri-substituted) aliphatic olefins.[2c,d] This decreased reactivity of styrene as compared with other olefins could indicate that different mechanisms of oxygen transfer are implicated in the hypochlorite and persulphate systems. This difference is also reflected in *cis*-stilbene epoxidation. Indeed, in the absence of pyridine, a *cis*:*trans* epoxide ratio of 35:65 was obtained with Mn(tpp)OAc–NaOCl,[2d] whereas with Mn(tpp)OAc–$KHSO_5$ this ratio is 87:13. In the presence of pyridine, a ratio of *ca.* 95:5 was obtained in both cases.

The Mn(tF_5pp)Cl–$KHSO_5$ combination can be compared favourably with acetone-catalysed epoxidation by $KHSO_5$, whereby cyclohexene was converted into the epoxide in about 80% yield after 3—4 h, and 1,2-epoxydodecane was formed in 45% yield from dodec-1-ene in 3 h.[14]

As sodium perborate has been recently reported to oxidise anilines and sulphides,[16a] we examined whether this reagent could also be used as a mono-oxygen donor for olefin epoxidation. This appeared not to be the case, as no consumption of olefin was observed in the systems oct-1-ene–Mn(tF_5pp)Cl–aqueous perborate or cyclohexene–Mn(tpp)OAc–aqueous perborate. Instantaneous gas evolution observed upon addition of the perborate solution to the organic phase makes us believe that in these systems the decomposition of the oxidant is the fastest process. One might also bear in mind that perborate behaves in aqueous solutions as a mixture of borate and hydrogen peroxide.[16b] Since the latter oxidant is inefficient as an oxygen donor in metalloporphyrin-catalysed epoxidations, it is not surprising that sodium perborate is not suitable as oxidant in the present case. For the two oxidants, NaOCl and $KHSO_5$, the presence of a good leaving group, Cl^- or HSO_4^-, probably makes easier the formation of Mn=O from the corresponding anions OCl^- and HSO_5^- after their co-ordination on the metal.

Conclusion

Porphyrinatomanganese(III) complexes can be used as catalysts for terminal olefin epoxidation with good selectivity in the presence of hypochlorite or potassium hydrogen peroxomonosulphate, when the *meso*-positions are substituted by phenyl groups bearing at least one *ortho*-substituent. The influence of this substituent seems to be largely due to steric interactions with the olefin and the catalytically active oxo-manganese species.

Experimental

G.l.c. analyses were performed with an Intersmat IGC 120 DFL instrument equipped with a capillary column (Chrompack CP WAX 51; 25 m × 0.22 mm); peak areas were measured with an Intersmat ICR-1B integrator. U.v.–visible spectra were obtained with a Cary 14 spectrophotometer.

Authentic samples of epoxides were prepared by epoxidation with *m*-chloroperbenzoic acid.[17]

Hypochlorite Solutions.—Sodium hypochlorite solutions used for the runs in Table 1 were purchased from Prolabo (Rectapur quality; [NaOCl] 0.20—0.34 mol dm^{-3}; [NaOH] undetermined).

Lithium hypochlorite solutions ([LiOCl] *ca.* 0.30 mol dm^{-3}) were prepared by dissolving solid LiOCl (Fluka, technical) in aqueous NaOH. Hypochlorite and hydroxide concentrations were determined titrimetrically.

For an unknown reason, non-commercial sodium hypochlorite solutions (made by passing Cl_2 into NaOH solution[18]) gave much lower selectivities.

The calcium hypochlorite solution was made from solid $Ca(OCl)_2$ (Fluka) and water. After filtration, the hypochlorite concentration was determined titrimetrically. When needed, NaF (*ca.* 1 equiv. *vs.* OCl^-) was added to the $Ca(OCl)_2$ solution, and the resulting milky mixture used without further treatment.

Porphyrins and Manganese Complexes.—Porphyrins were prepared according to published procedures: (tF_5pp)H_2,[19] (*p*Trifpp)H_2,[20] (*p*Fpp)H_2,[21] (*o*Fpp)H_2,[21] (*o*Clpp)H_2,[21] and (tCl_2pp)H_2.[21] In the cases of (*o*Fpp)H_2 and (*p*Fpp)H_2 the solid that precipitated from the reaction mixture was used in the metallation reaction without further purification [owing to its low solubility (*p*Fpp)$\mathrm{H_2}$ could not be chromatographed]. In the cases of (*p*Trifpp)$\mathrm{H_2}$ and (*o*Clpp)$\mathrm{H_2}$, the solid which precipitated was filtered off, washed with hot water and MeOH, and chromatographed on $\mathrm{Al_2O_3}$ (dry column chromatography) with $\mathrm{CHCl_3}$.

In the synthesis of $(\mathrm{tF_5pp})\mathrm{H_2}$, no solid precipitated. Therefore, the propionic acid was evaporated off *in vacuo*, and the black slurry dissolved in $\mathrm{CH_2Cl_2}$–light petroleum (1:1) and chromatographed on $\mathrm{Al_2O_3}$ with $\mathrm{CH_2Cl_2}$–light petroleum (30:70). The first red-brown band was the desired porphyrin.

Chromatography on $\mathrm{Al_2O_3}$ (with $\mathrm{CH_2Cl_2}$–light petroleum mixtures) yielded an impure sample of $(\mathrm{tCl_2pp})\mathrm{H_2}$ (maximum yield 0.5%) which was metallated. After chromatography ($\mathrm{Al_2O_3}$; $\mathrm{CHCl_3}$) the $\mathrm{Mn(tCl_2pp)Cl}$ was not completely pure (several spots on t.l.c.). The epoxidation was performed with this impure sample: its visible spectra ($\mathrm{CHCl_3}$) were similar to the spectra of the other complexes (see later).

Incorporation of manganese was performed as described.[22] The manganese complexes were purified by dry column chromatography on neutral aluminium oxide with chloroform as eluant.

$\mathrm{Mn(tF_5pp)Cl}$ (Found: C, 50.5; H, 1.1; N, 5.4. $\mathrm{C_{44}H_8ClF_{20}MnN_4}$ requires C, 49.7; H, 0.9; N, 5.3%); $\lambda_{\max.}$ (log ε) ($\mathrm{CH_2Cl_2}$) 573 (4.02) with short-wavelength shoulder, 474 (4.94), and 364 nm (4.80).

Mn(*p*Fpp)Cl·0.5$\mathrm{CHCl_3}$ (Found: C, 64.3; H, 2.9; N, 6.1. $\mathrm{C_{44.5}H_{24.5}Cl_{2.5}F_4MnN_4}$ requires C, 64.0; H, 3.0; N, 6.7%); $\lambda_{\max.}$ (log ε) ($\mathrm{CHCl_3}$) 616 (3.94), 581 (3.93), 527 (3.65), 477 (5.01), and 375 nm (4.73) with a high- and a low-wavelength shoulder.

Mn(*p*Trifpp)Cl (Found: C, 60.4; H, 2.4; N, 5.1 $\mathrm{C_{48}H_{24}ClF_{12}MnN_4}$ requires C, 59.1; H, 2.5; N, 5.7%); $\lambda_{\max.}$ (log ε) ($\mathrm{CHCl_3}$) 615 (3.92), 581 (4.00), 526 (3.69), 478 (5.10), and 373 nm (3.78) with a high- and a low-wavelength shoulder.

Mn(*o*Fpp)Cl·$\mathrm{CHCl_3}$ (Found: C, 61.4; H, 2.5; N, 5.7. $\mathrm{C_{45}H_{25}Cl_4F_4MnN_4}$ requires C, 60.4; H, 2.8; N, 6.3%); $\lambda_{\max.}$ (log ε) ($\mathrm{CH_2Cl_2}$) 611 (3.86), 577 (4.03), 525 (3.71), 475 (5.13), and 371 nm (4.78), with a high- and a low-wavelength shoulder.

Mn(*o*Clpp)Cl (Found: C, 63.0; H, 2.7; N, 6.1. $\mathrm{C_{44}H_{24}Cl_5MnN_4}$ requires C, 62.8; H, 2.9; N, 6.7%); $\lambda_{\max.}$ (log ε) ($\mathrm{CH_2Cl_2}$) 612 (3.78), 579 (4.01), 523 (3.71), 476 (5.10), and 370 nm (3.78), with a high- and a low-wavelength shoulder.

General Procedure for the Epoxidation with LiOCl.—As an example, we describe the procedure for the epoxidation of oct-1-ene with Mn(*o*Fpp)Cl. In a small Schlenk tube, Mn(*o*Fpp)Cl·$\mathrm{CHCl_3}$ (0.010 mmol), benzyldimethyltetradecylammonium chloride (0.026 mmol), pyridine (0.20 mmol), and oct-1-ene (1.28 mmol; passed through a small column of aluminium oxide before use) were dissolved in methylene dichloride (3 ml). Aqueous 0.28M-LiOCl (10 ml) was added, and the mixture was stirred at room temperature. The reaction was followed by analysing 1 μl samples of the organic phase by g.l.c. after 0.5, 0.75, and 1 h, at which time less than 10% of oct-1-ene remained. After 1 h, the two phases were separated and the organic phase was added to dodecane (39.0 mg) as g.l.c. reference.

Epoxidation of Propene.—$\mathrm{Mn(tF_5pp)Cl}$ (0.010 mmol) and benzyldimethyltetradecylammonium chloride (0.027 mmol) were put in a Schlenk tube, which was then evacuated. The tube was filled with gaseous propene (*ca.* 50 ml) by means of a syringe provided with a metallic stop-cock. Methylene dichloride (3 ml), pyridine (0.20 mmol), and aqueous NaOCl (0.3 M; 9 ml) were added through a septum. After 3 h, analysis by g.l.c. showed the absence of propene. After separation of the phases and drying of the organic phase on $\mathrm{Na_2SO_4}$, 1,2-epoxybutane was added as the g.l.c. reference.

Control of the Stability of 1,2-*Epoxyoctane in the Reaction Medium.*—Mn(*o*Clpp)Cl (0.010 mmol), benzyldimethyltetradecylammonium chloride (0.027 mmol), 1,2-epoxyoctane (0.52 mmol), pyridine (0.20 mmol), and hex-1-ene (1.59 mmol; passed over $\mathrm{Al_2O_3}$) were added to a small Schlenk tube and dissolved in $\mathrm{CH_2Cl_2}$ (3 ml). Lithium hypochlorite (0.28M; 4.5 ml, 1.26 mmol) was added and the mixture was stirred until the hypochlorite was completely consumed. Work-up and analysis were performed as in the general procedure; 91% of the starting 1,2-epoxyoctane was present. With $\mathrm{Mn(tF_5pp)Cl}$ and Mn(*p*-Trifpp)Cl, 89% of the epoxide remained.

Epoxidation with Persulphate.—In a typical experiment, Mn(tpp)OAc (0.006 mmol), benzyldimethyltetradecylammonium chloride (0.024 mmol), and cyclohexene (0.40 mmol) were dissolved in $\mathrm{CH_2Cl_2}$ (1.5 ml). A *ca.* 0.25M-$\mathrm{Na_2HPO_4}$–$\mathrm{NaH_2PO_4}$ buffer solution of pH 8 (20 ml) and 'oxone' (Alfa, 0.3 g, corresponding to *ca.* 0.84 mmol of $\mathrm{KHSO_5}$) were added, and the mixture was stirred at room temperature. The g.l.c. analysis was performed as for the LiOCl epoxidation.

Attempted Epoxidation with Sodium Perborate.—In a typical experiment, Mn(tpp)OAc (0.011 mmol), benzyldimethyltetradecylammonium chloride (0.027 mmol), cyclohexene (1.48 mmol), and pyridine (0.23 mmol) were dissolved in $\mathrm{CH_2Cl_2}$ (3 ml). A solution of sodium perborate (919 mg) in water (10 ml) was added, which caused gas evolution, and the mixture was stirred at room temperature for 3 h. Analysis by g.l.c. showed no epoxide and virtually no consumption of cyclohexene. Addition of HCl to the aqueous solution (to pH 7—8) prior to its addition to the organic phase did not alter the outcome of the reaction.

References

1 (*a*) J. T. Groves and T. E. Nemo, *J. Am. Chem. Soc.*, 1983, **105**, 5786, 6243; (*b*) J. T. Groves and R. S. Myers, *ibid.*, p. 5791; (*c*) J. R. Lindsay Smith and P. R. Sleath, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1009; 1983, 1165; (*d*) C. J. Chang and F. Ebina, *J. Chem. Soc., Chem. Commun.*, 1981, 778; (*e*) C. L. Hill, J. A. Smegal, and T. J. Henly, *J. Org. Chem.*, 1983, **48**, 3277.

2 (*a*) I. Tabushi and N. Koga, *Tetrahedron Lett.*, 1979, 3681; (*b*) E. Guilmet and B. Meunier, *ibid.*, 1980, **21**, 4449; (*c*) E. Guilmet and B. Meunier, *Nouv. J. Chim.*, 1982, **6**, 511; (*d*) B. Meunier, E. Guilmet, M.-E. De Carvalho, and R. Poilblanc, *J. Am. Chem. Soc.*, 1984, **106**, 6668; (*e*) J. P. Collman, J. I. Bravman, B. Meunier, S. A. Rayhuck, and T. Kodadek, *Proc. Natl. Acad. Sci. USA*, 1984, **81**, 3245.

3 M. W. Nee and T. C. Bruice, *J. Am. Chem. Soc.*, 1982, **104**, 6123.

4 T. Takata and W. Ando, *Tetrahedron Lett.*, 1983, **24**, 3631.

5 (*a*) H. J. Ledon, P. Durbot, and F. Varescon, *J. Am. Chem. Soc.*, 1981, **103**, 3601; (*b*) D. Mansuy, J.-F. Bartoli, and M. Momenteau, *Tetrahedron Lett.*, 1982, **23**, 2781; (*c*) D. Mansuy, P. Battioni, and J.-P. Renard, *J. Chem. Soc., Chem. Commun.*, 1984, 1255.

6 I. Tabushi and A. Yazaki, *J. Am. Chem. Soc.*, 1981, **103**, 7371.

7 D. Mansuy, M. Fontecave, and J.-F. Bartoli, *J. Chem. Soc., Chem. Commun.*, 1983, 253.

8 (*a*) I. Tabushi and N. Koga, *J. Am. Chem. Soc.*, 1979, **101**, 6456; (*b*) M. Perrée-Fauvet and A. Gaudemer, *J. Chem. Soc., Chem. Commun.*, 1981, 874; (*c*) I. Tabushi and K. Morimitsu, *J. Am. Chem. Soc.*, 1984, **106**, 6871.

9 B. Meunier, *Bull. Soc. Chim. Fr.*, 1983, II-345.

10 B. De Poorter and B. Meunier, *Tetrahedron Lett.*, 1984, **25**, 1895.

11 A. W. Van Der Made, J. W. H. Smeets, R. J. M. Nolte, and W. Drenth, *J. Chem. Soc., Chem. Commun.*, 1983, 1204.

12 P. S. Traylor, D. Dolphin, and T. G. Traylor, *J. Chem. Soc., Chem. Commun.*, 1984, 279.

13 B. M. Trost and D. P. Curran, *Tetrahedron Lett.*, 1981, **22**, 1287.

14 G. Cicala, R. Curci, M. Fiorentino, and O. Laricchiuta, *J. Org. Chem.*, 1982, **47**, 2670.

15 W. Ando, H. Miyazaki, and T. Akasaka, *J. Chem. Soc., Chem. Commun.*, 1983, 518.

16 (*a*) A. McKillop and J. A. Tarbin, *Tetrahedron Lett.*, 1983, **24**, 1505; (*b*) 'Nouveau Traité de Chimie Minérale,' ed. P. Pascal, Masson, Paris, 1961, vol. VI, p. 223.

17 L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' Wiley, New York, 1967, vol. I, p. 136.

18 F. B. Mallory, *Org. Synth.*, 1957, **37**, 1.

19 F. R. Longo, M. G. Finarelli, and J. B. Kim, *J. Heterocycl. Chem.*, 1969, **6**, 927.

20 S. S. Eaton and G. R. Eaton, *J. Am. Chem. Soc.*, 1975, **97**, 3660.

21 J. B. Kim, J. J. Leonard, and F. R. Longo, *J. Am. Chem. Soc.*, 1972, **94**, 3986.

22 R. D. Jones, D. A. Summerville, and F. Basolo, *J. Am. Chem. Soc.*, 1978, **100**, 4416.

23 R. A. Sheldon and K. Kocki, 'Metal-catalyzed Oxidations of Organic Compounds,' Academic Press, New York, 1981.

Received 31*st January* 1985; *Paper* 5/165