5,10,15,20-Tetrakisaryl- and 2,3,7,8,12,13,17,18-Octahalogeno-5,10,15,20-tetrakisarylporphyrins and their Metal Complexes as Catalysts in Hypochlorite Epoxidations

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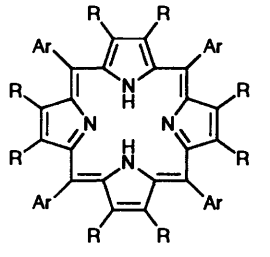
Improvements are described to the synthesis of the catalytically important 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin **1** (R = H) and [2,3,7,8,12,13,17,18-octachloro-tetrakis(2,6-dichlorophenyl)porphyrinato]manganese(III) **3** (R = Cl) which enable large-scale preparation of such compounds to be carried out easily. A comparative study of the catalytic performance of the manganese complexes of these two porphyrins proved that, contrary to earlier expectations, the manganese complex of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin is the most stable and efficient catalyst for epoxidation when using sodium hypochlorite as oxidant. With [2,3,7,8,12,13,17,18-octachloro-tetrakis(2,6-dichlorophenyl)porphyrinato]manganese(III) **3**, chlorinated products tend to be formed and these can be the dominant products for some substrates.

The search for a suitable model metalloporphyrin to act as a biomimetic counterpart to the multiple fundamental biological roles played by iron protoporphyrin-IX has led to many diverse studies in recent years.[1] Owing to the easy synthetic availability of the manganese and iron complexes of 5,10,15,20-tetrakisphenylporphyrin (TPP),† these were the first catalysts to be used to mimic the action of oxidative metalloenzymes.[2] The extremely low stability of those metallocomplexes to the reaction conditions employed, soon led to 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin **1** (R = H; TDCPP) becoming the porphyrin of choice because of its greater stability during the oxidation of hydrocarbons with a variety of oxygen donors.[3] The originally difficult Rothemund–Adler synthesis of TDCPP has been improved recently.[4] As a further development, 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin **1** (R = Br) was synthesized and its catalytic



Ar = $C_6H_3Cl_2$-2,6

1 R = H (TDCPP); R = Cl or Br (TDCPPCl$_8$)
2 R = H (Mn complex of TDCPP)
3 R = Cl (Mn complex of TDCPPCl$_8$)

activity towards epoxidation with iodosobenzene as oxygen donor was investigated.[5] It was reported that this octabromo derivative was an efficient and stable catalyst. These last experiments were performed in the presence of such a large excess of substrate relative to the oxidant that the alkene substrate appeared to protect the porphyrin from oxidation. Later, other publications appeared on the use of β-perhalogenated porphyrins as catalysts with iodosobenzene, potassium peroxysulphate, magnesium monoperoxyphthalate or H_2O_2 as oxygen donors.[6] Notably, with hydrogen peroxide, when the reaction was performed using equimolar amounts of oxidant and alkene substrate, it was observed that 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin **1** (R = Cl; TDCPPCl$_8$) as its manganese complex, although acting as a powerful catalyst for the oxidation of alkenes, was inefficient in turnover number, being rapidly and completely destroyed during the course of the catalysed epoxidation.[7]

Because of their powerful catalytic properties, the manganese complex **2** of TDCPP **1** (R = H) and the manganese complex **3** of TDCPPCl$_8$ **1** (R = Cl) have been and are being used widely in further studies. Although they are available through the methods listed above, large-scale syntheses of both porphyrins are still difficult and expensive. In the present work, significant improvements to the synthesis of these porphyrins are described such that large-scale preparation becomes relatively straightforward. Further, their catalytic activity towards epoxidation of a variety of alkenes has been exploited, using sodium hypochlorite as oxygen donor in a biphasic solvent system.

Results and Discussion

(a) *Synthesis of Porphyrins.*—Preliminary studies had shown that, for optimum yields, condensation of an alkanal and pyrrole to the porphyrinogen stage needed to be separated from the subsequent oxidation step to the porphyrin level.[8] This two-step approach was later extended to the synthesis of several 5,10,15,20-tetrakisarylporphyrins.[9] Significantly, different conditions must be met in each of these steps if the synthesis is to be successful overall. In their original form, the syntheses were performed under conditions of very high dilution and required the use of expensive quinones, such as 2,3-dichloro-5,6-dicyanobenzoquinone, and involved laborious and time-consuming final purification. Other research revealed that several 5,10,15,20-tetrakisarylporphyrins could be synthesized successfully in a one-pot reaction through use of a mixture of a carboxylic acid and nitrobenzene as reaction solvent.[4] The synthesis of TDCPP **1** (R = H) through this one-pot reaction proved, at the time, to be the most convenient procedure, although the yield never exceeded 5–6%. The considerable advantage of this method lay in the fact that the porphyrin was obtained in crystalline form directly from the reaction medium; the costs in solvents, reagents and work-up

† Generally, the term *meso* is used to refer to the 5,10,15,20 positions and β to the 2,3,7,8,12,13,17,18 positions.

Table 1 Some typical reaction conditions for complete conversion of *cis*-cyclooctene into epoxide, using NaOCl and a manganese porphyrin catalyst[a]

Porphyrin catalyst 2 [Mn(TDCPP)] or 3 [Mn(TDCPPCl$_8$)]	pH	Reaction time (h)	Porphyrin remaining (%)
2	12–13[b]	7	98
2	10.5[b]	0.5	100
3	12–13[c]	12	*d*
3	10.5[c]	7	*d*

[a] Reaction conditions are reported in the Experimental section. [b] Ratio of pyridine:porphyrin = 5:1. [c] Ratio of pyridine:porphyrin = 25:1. [d] The Soret band for the starting material could not be measured because of the persistence of an interfering band from another porphyrin-like material absorbing at 448 nm.

times are very advantageous in comparison with any other method. The usefulness of the porphyrins outlined above as catalysts prompted an investigation into improvements to the synthetic procedures.

After mixing equivalent quantities of pyrrole and 2,6-dichlorobenzaldehyde with BF_3 in $CHCl_3$ or CH_2Cl_2 as described,[9] it was found, by oxidation of small trial aliquots with 2,3-dichloro-5,6-dicyanoquinone (DDQ), that the Soret band for porphyrin reached a maximum after about 3 h. Neutralization of the BF_3 with triethylamine followed by addition of aqueous hydrogen peroxide in acetic acid afforded TDCPP in 20% yield; ^{1}H NMR spectroscopy revealed no bands between δ 8 and 9 characteristic of the corresponding chlorin. The method is being extended to other porphyrins and oxidants.

A previously established procedure[7] for the preparation of β-perhalogenated TDCPP through light-catalysed halogenation using the required *N*-halogenosuccinimide is not the most amenable for large-scale preparations, essentially because of the large dilutions required and the need for strong light sources. It was decided to exploit the possibility of carrying out β-chlorination of manganese porphyrin **2** using conditions similar to those reported for Fe(TDCPP).[10] Bubbling chlorine gas through a solution of Mn(TDCPP) **2** in *o*-dichlorobenzene at 120 °C containing a trace of anhydrous $FeCl_3$ led to extremely fast disappearance of the Soret band. This suggested at first that the porphyrin had been destroyed but further observation revealed that, by keeping the solution for a further 3 h with continued passage of more chlorine gas, a new Soret band developed at 498 nm characteristic of Mn(TDCPPCl$_8$) **3**. Work-up of this solution gave an isolated yield of 75%. Complementary studies of similar halogenations with nickel and zinc complexes of TDCPP allowed for an efficient β-chlorination of the TDCPP macrocycle. Extended studies of this halogenation method, including clarification of the mechanism and identification of the isolated intermediate having no Soret band are under way.

(b) *Epoxidation of Alkenes.*—Earlier attempts to use Mn(TDCPPCl$_8$) **3** as an oxidation catalyst were very promising but published results[11,12] provided evidence of poor selectivity and poor stability of the catalyst. Application of H_2O_2 as oxidant in a homogeneous system suggests that both problems originate from the formation of very reactive radical species.[7] In order to clarify the situation it was decided to carry out a comparative study of the activities and stabilities of manganese complexes **2**, **3** in a biphasic solvent system, with NaOCl as oxygen donor. Previous reports of oxidations with NaOCl indicate that reaction rates are critically dependent on the pH of the aqueous phase.[13] Therefore, the influence of pH on the epoxidation of *cis*-cyclooctene was studied for both catalyst **2** and **3**. Results are given in Table 1. It was confirmed that there was a pronounced influence of pH on the rate of epoxidation when catalyst **2** was used, even in the alkaline range. For example, changing the pH from 12.5 to 10.5 reduced the reaction time from 7 to 0.5 h. Although there was a variation in rate when catalyst **3** was used over the same range of pH, the magnitude of the change was much smaller. Also, it was observed that both catalysts required the presence of an axial ligand such as pyridine for efficient activity. Again, there was a difference in the behaviour between catalysts **2** and **3**. With Mn(TDCPP) **2**, the greatest reaction rate was obtained with a pyridine-to-porphyrin ratio of 5:1, whilst for porphyrin **3**, the optimum ratio was 25:1. These results show that, for the case of hypochlorite oxidation in a biphasic system, one catalyst **2** is more efficient than the other **3**. Under equivalent conditions, Mn(TDCPP) catalyses the complete conversion of *cis*-cyclooctene into its epoxide at a far greater rate than does the more chlorinated one **3**. Also, the former porphyrin is recovered almost completely at the end of the reaction (Table 1). It is notable that porphyrin **3** is converted into another material having a visible (Soret) absorption band at 448 nm (Table 1). Thus, at the end of reaction when all alkene has been converted, porphyrin **3** is not recovered and nor is it recovered if more alkene is added. The 448 nm band seen with catalyst **3** appears to be the equivalent of a band at 422 nm, reported[14] for the Mn-OCl coordination complex of compound **2**. If this supposition is correct, the red shift observed must be due to the presence of the eight β-chlorine atoms. On addition of an excess of alkene substrate at the end of reaction, the 448 nm band slowly fades but only with partial conversion back into structure **3**. Apparently, the stability of the Mn-OCl derivative of catalyst **3** leads to a decrease in its catalytic activity because the complex disfavours the formation of the required intermediate oxidation state, $Mn^V = O$. At the end of epoxidation with porphyrin **2**, an absorption at 417 nm appears in place of the Soret band usually observed in the presence of an excess of NaOCl; this band instantaneously reverts to the original Soret absorption of **2** on addition of more alkene at the end of the reaction. This major difference between the two manganese complexes **2**, **3** indicates that the presence of eight β-chlorine atoms is a disadvantage for catalytic epoxidation, *at least with sodium hypochlorite as oxidant.*

An attempt was made to overcome the poor catalytic activity of porphyrin **3** relative to **2** by replacing the pyridine ligand used in the experiments described above by a more effective donor which could favour the formation of the required Mn^V-oxo intermediate. For this purpose, the series pyridine, 4-methylpyridine and 2,4,6-trimethylpyridine was examined for its effect on the epoxidation of one alkene, styrene. Table 2 summarizes the results of these experiments. As might have been expected, 4-methylpyridine, a better donor ligand, changed the efficiency of both catalysts **2**, **3** relative to the effect of pyridine but not uniformly. The perchlorinated catalyst **3** remained less efficient than the other, under these more favourable conditions.

The effectiveness of both porphyrins **2**, **3** as catalysts for epoxidation was more extensively compared in a series of experiments in which 4-methylpyridine was used as axial ligand but with a variety of alkenes. Table 3 compares the results and shows evidence for consistently greater activity and better selectivity towards epoxidation of porphyrin **2** relative to **3**. As expected, the lower catalytic activity of compound **3** for epoxidation makes reactions with it slower and, where this catalyst is used, the starting materials and products are prone to generate secondary materials. These include not only different oxidation products originating from rearrangements of the epoxide but also chlorinated compounds from alternative reaction pathways. The identified products give evidence that porphyrin **3** has chloroperoxidase activity, as has been observed

Table 2 Epoxidation of styrene using Mn(TDCPP) or Mn(TDCPPCl$_8$) with various axial pyridine ligands[a]

Porphyrin catalyst 2 [Mn(TDCPP)] or 3 [Mn(TDCPPCl$_8$)]	Axial ligand	Reaction time[b] (h)	Yield of epoxide (%)
None	4-Methylpyridine	5	0
2	None	4	90
2	Pyridine[c]	0.5	91
2	4-Methylpyridine[c]	0.30	90
2	2,4,6-Trimethylpyridine[c]	3	90
3	None	9	80
3	Pyridine[d]	6	73
3	4-Methylpyridine[d]	2.5	70
3	2,4,6-Trimethylpyridine[d]	9	60
None	2,4,6-Trimethylpyridine[d]	20	9[e]

[a] Reaction conditions are reported in the Experimental section. [b] Time required for complete conversion of the substrate. [c] Ratio of pyridine:porphyrin = 5:1. [d] Ratio of pyridine:porphyrin = 25:1. [e] Complex mixture of products.

Table 3 Oxidation of alkenes using NaOCl as oxygen donor and 4-methylpyridine as axial ligand[a]

Porphyrin catalyst 2 [Mn(TDCPP)] or 3 [Mn(TDCPPCl$_8$)]	Alkene	Reaction time (h)	Yield of epoxide[b] (%)	Other products observed (%)
2[c]	Styrene	0.3	88 (87)	12[e]
3[d]	Styrene	2.5	70	30[f]
2[c]	*cis*-Cyclooctene	0.5	95 (92)	5
3[d]	*cis*-Cyclooctene	3	80	20
2[c]	*cis*-Stilbene	0.3	70 (90)[g]	30
3[d]	*cis*-Stilbene	1	50	50[h]
2[c]	*trans*-Stilbene	24	—	—
3[d]	*trans*-Stilbene	24	28	72[i]
2[c]	Oct-1-ene	1	90 (75)	10
3[d]	Oct-1-ene	4	10	20[j]

[a] Reaction conditions are reported in the Experimental section. [b] Percentages are based on simple GC peak areas; isolated yields are quoted in parentheses. [c] Pyridine to porphyrin ratio = 5:1. [d] Pyridine to porphyrin ratio = 25:1. [e] The estimated yield of phenylacetaldehyde was about 10%. [f] The main products are mono-chlorinated derivatives. [g] On isolating the reaction product at the end of the reaction, a mass yield of 90% was obtained. The ^{1}H NMR spectrum of this material showed that it was 83% of *cis*-stilbene epoxide and 17% of diphenylacetaldehyde. [h] A mixture of diphenylacetaldehyde and chlorinated products was identified by GC/MS methods. [i] A complex mixture of chlorinated and oxo products was obtained (GC/MS), with even some Bayer-Villiger rearrangement product being detected also. [j] There was a 30% conversion of alkene into products of which the dominant one was 1,2-dichlorooctane.

already by others with other metalloporphyrins that lead to chlorination of substrate.[15] This chlorination activity can be dominant, as was observed in the case of oct-1-ene which gave 1,2-dichlorooctane as the main product. Another example deserving special comment is the reaction with *trans*-stilbene. Catalyst **2**, having *ortho* chloro substituents but hydrogen at the β-pyrrole positions is unable to promote any reaction with *trans*-stilbene. In contrast, catalyst **3**, with chlorines at both the *ortho* and β-positions leads to complete conversion of stilbene to products of which only 28% is epoxide. Thus, steric hindrance does not appear to prevent reaction of stilbene with the more highly substituted catalyst **3** as it does with **2** and a different mechanism must be operating. In all earlier reports on oxidation, *trans*-stilbene has been used as a probe for mechanistic conclusions concerning metalloporphyrin catalysis. In many reported oxidations of stilbene catalysed by metalloporphyrins, a low yield of epoxide has been thought to be due to difficulties in the approach of the bulky *trans*-stilbene to the metallo-oxo centre.[16] In the present instance with catalyst **3**, there is relatively little epoxidation but, nevertheless, it is the major single product and retains its stereochemistry. Through competing processes because of slow reaction, a variety of secondary products is formed, many of them arising from opening of the first-formed epoxide ring. Thus, taking these ring-opened products into account, the yield of epoxide is actually quite high. It is not clear how the more highly substituted porphyrin **3** can lead to epoxidation when the less substituted **2** does not if steric hindrance is to be invoked[16] as the reason for poor yields and probably an alternative mechanism is operative.

Conclusion

New approaches to the synthesis of TDCPP **1** (R = H) and Mn(TDCPPCl$_8$) **3** have made these important compounds easily accessible on a preparative scale. With these new approaches, the availability and cost of TDCPP is now similar to that of TPP. Also, simple β-chlorination of Mn(TDCPP) was made possible on a preparative scale with inexpensive reagents and an easy work-up procedure. A comparative study between the catalytic performances of Mn(TDCCP) and Mn-(TDCPPCl$_8$) towards epoxidation proved that the former is the best catalyst when the oxygen donor is sodium hypochlorite. The presence of the eight β-chlorine atoms does not provide stability to the catalyst, even under the protecting conditions created by a biphasic system; the catalytic activity of porphyrin **3** is consistently less than that of **2**. The lower catalytic activity towards epoxidation makes the selectivity of catalyst **3** always worse than that of **2** with almost all alkenes shown in Table 3. Only in the case of *trans*-stilbene is catalyst **3** active whilst **2** is totally inactive although the reaction is slow and selectivity is poor. In some cases, substantial amounts of chlorinated

materials resulting from attack by Cl^- on the epoxide or Cl^+ on the alkene were found on GC/MS examination of the products of reaction, particularly the slower reactions in which the perchlorinated catalyst **3** was used (Table 3).

Experimental

All solvents and reagents were purified by standard methods before use. For the identification of the reaction products, the epoxides were prepared independently and characterized by the usual methods (NMR, MS, IR, *etc.*), all being known compounds. The epoxides were identified by comparison of their chromatographic retention times and mass spectra with authentic materials; the other reaction products were identified through their mass spectra and comparison against library references. Catalytic reactions were monitored by removing aliquots at intervals and examining the products by gas chromatography. In the tables, measured relative peak areas are reported without any allowance for differential detection efficiency.

The NaOCl solution (0.35 mol dm^{-3}; pH = 10.5) was prepared from a concentrated one (0.68 mol dm^{-3}) by adjusting the pH with 10% HCl and subsequent dilution. The pH of the NaOCl solution was measured using a Metrohm 620 pH-Meter equipped with a combined glass electrode.

^1H NMR spectra were recorded on a Varian XL200 at 200 MHz, using deuteriochloroform as solvent. Gas chromatography was carried out on a Hewlett-Packard 5890A instrument using a capillary column OV-1 (25 m × 0.3 mm, i.d.). Typically, a GC analysis was run at 55 °C for 1 min after which the temperature was increased at 20 °C min^{-1} up to 220 °C. For stilbenes the initial temperature was 100 °C. Gas chromatography–mass spectrometry was carried out using a Hewlett-Packard 5890 II gas chromatograph coupled to a 5970 B mass spectrometer with electron ionization at 70 eV or with a VG 7070 E machine, using a similar column and ionization conditions. Mass spectrometry was carried out on the VG 7070E mass spectrometer using FAB ionization with xenon and a 3-nitrobenzyl alcohol matrix. UV–VIS spectra were measured on an Hitachi-220 S spectrophotometer and on a Hewlett-Packard 235 CH 10609 spectrometer.

Porphyrin Syntheses.—5,10,15,20-*Tetrakis*(2,6-*dichlorophenyl*)*porphyrin* **1** (R = H). To a round-bottomed flask containing a solution of 2,6-dichlorobenzaldehyde (5 × 10^{-3} mol) in $CHCl_3$ (500 cm^3) was added pyrrole (5 × 10^{-3} mol) and BF_3·OEt_2 (5 × 10^{-4} mol) under nitrogen and with a minimum of light. As the reaction proceeded, formation of the maximum yield of porphyrinogen was monitored by oxidizing small aliquots with 2,3-dichloro-5,6-dicyanoquinone (DDQ) in toluene (10^{-2} mol dm^{-3}) and then immediately measuring the height of the Soret band above the general background level. When the Soret band had reached its maximum (after *ca.* 3 h), triethylamine (70 mm^3)* was added to quench the BF_3. To this solution was added a freshly prepared solution of acetic acid (*ca.* 100 cm^3) containing H_2O_2 (35% v/v; 2 cm^3) and the whole was set aside for 1 h. The mixture was then evaporated and the crude product was easily purified by chromatography on alumina (neutral Brockmann Grade II, Aldrich) using chloroform as eluent to give the required porphyrin (222 mg, 20%); $\delta_H(CDCl_3)$ 8.69 (8 H, s), 7.65–7.85 (12 H, m), −2.53 (2 H, br s); *m/z* (FAB) 887 ([M + H^+], 100%); $\lambda_{max}(CHCl_3)$/nm (% relative peak heights) 418 (100%), 512 (6), 587 (2), 611 (0.3) and 657 (0.2) (Found: C, 59.3, H, 2.5, N, 6.3. Calc. for $C_{44}H_{22}Cl_8N_4$: C, 59.3, H, 2.5, N, 6.3%).

* 1 mm^3 = 1 μl.

[5,10,15,20-*Tetrakis*(2,6-*dichlorophenyl*)*porphyrinato*]-*manganese*(III) *Chloride* **2**. Manganese was inserted into TDCPP, prepared as above, by a previously described method.[17] Purification by column chromatography on neutral alumina (Grade II, Merck) with chloroform to which methanol was gradually added as eluent gave the title compound (91%); *m/z* (FAB) 923 (100%) (Found: C, 53.4; H, 2.3; N, 5.3. Calc. for $C_{22}H_{20}Cl_8MnN_2$: C, 53.99; H, 2.06; N, 5.73%); $\lambda_{max}(CH_2Cl_2$–MeOH)/nm (relative peak heights) 478 (100%), 521 (2) and 578 (1.2).

2,3,7,8,12,13,17,18-*Octachloro*-5,10,15,20-*tetrakis*(2,6-*dichlorophenyl*)*porphyrinato*)*manganese*(III) *Chloride* **3**.—To a solution of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin-manganese(III) chloride (5.10 × 10^{-3} mmol) in *o*-dichlorobenzene (10 cm^3) at 120 °C was added anhydrous $FeCl_3$ (2 mg); gaseous chlorine was then bubbled into the solution. On checking the reaction by UV–VIS spectroscopy, it was observed that, after 5 min, the Soret band disappeared completely. When the reaction mixture was maintained at 120 °C for 3 h, a new Soret band at 498 nm appeared. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel-60 (Merck) with $CHCl_3$–MeOH (10:1) as eluent to give compound **3** (0.048 g, 75%) as a crystalline powder; *m/z* (FAB) 1219 (M^+), the pattern of isotope peaks was correct for a compound having 16 Cl, the molecular ion isotope peaks being in the range *m/z* 1211–1240 with maxima at 1219 (100%) and 1221 (99%); $\lambda_{max}(CHCl_3)$/nm (% relative peak heights) 497 (100%), 605 (11) and 641sh. This chlorinated porphyrin was also prepared by chlorination with *N*-chlorosuccinimide and light.[18]

General Procedure for Oxidations using Sodium Hypochlorite as Oxygen Donor.—In a typical reaction (Table 3), the alkene (1 mmol), the requisite manganese porphyrin **2** (5 × 10^{-3} mmol), 4-methylpyridine (2.5 × 10^{-2} mmol) and trimethylnonylammonium bromide (1 × 10^{-2} mmol) were dissolved in $CHCl_3$ (1.5 cm^3). Aqueous NaOCl (9 cm^3) was added at room temperature to the stirred mixture. The reaction was monitored by GC to complete disappearance of the substrate alkene. For the manganese porphyrin **3**, the same procedure was used except for the amount of 4-methylpyridine (1.25 × 10^{-1} mmol) used. For the experiments relating to Tables 1 and 2, the same procedure was used but with the listed pyridines and pH values.

Procedure for Oxidations using Sodium Hypochlorite as Oxygen Donor on a Preparative Scale.—Authentic epoxides were prepared by literature methods: styrene epoxide;[19,20] *cis*-cyclooctene epoxide;[21] oct-1-ene epoxide;[22] *cis*-stilbene epoxide.[23]

Epoxidation of styrene. Styrene (2 mmol), manganese porphyrin **2** (1 × 10^{-2} mmol) and pyridine (1.5 × 10^{-2} mmol) were dissolved in $CHCl_3$ (3 cm^3) and treated with aqueous NaOCl (18 cm^3); the mixture was stirred until the substrate had completely disappeared (30 min). The mixture was then diluted with $CHCl_3$ (10 cm^3) and the organic phase removed, washed with water (×3) and dried (Na_2SO_4). The solution was concentrated and the residue was chromatographed (SiO_2; CH_2Cl_2–hexane, 9:1 as eluent) to yield styrene epoxide (0.216 g, 90%); *m/z* (GC/MS) 120 (M^+); δ_H 7.27–7.29 (5 H, m), 3.80–3.83 (1 H, m), 3.07–3.12 (1 H, m) and 2.73–2.77 (1 H, m).

Epoxidation of cis-*cyclooctene.* Using the procedure described above but with *cis*-cyclooctene in place of styrene gave *cis*-cyclooctene epoxide (0.232 g, 92%); *m/z* (GC/MS) 126 (M^+); δ_H 1.23–1.74 (10 H, m), 2.16–2.25 (2 H, m) and 2.92–2.97 (2 H, m).

Epoxidation of oct-1-ene. Using the procedure described above but with oct-1-ene in the presence of pyridine (3 × 10^{-2}

mmol) afforded oct-1-ene epoxide (0.192 g, 75%) as an oil; *m/z* (GC/MS) 128 (M^+); δ_H 0.80–1.0 (3 H, m), 1.21–1.63 (10 H, m), 2.22–2.54 (1 H, m), 2.73–2.81 (1 H, m) and 2.92 (1 H, br s).

Epoxidation of cis-*stilbene*. Using the procedure described above but with *cis*-stilbene gave an oil (0.196 g, 90%) which proved to be a mixture of *cis*-stilbene epoxide and diphenylacetaldehyde (from ^1H NMR integrals: the ratio of the area of epoxide H at δ 4.23 to the area of Ph_2CH in the aldehyde at δ 4.88 is 4.8:1 or 83:17). *cis*-Stilbene oxide, *m/z* (GC/MS) 196 (M^+); diphenylacetaldehyde, *m/z* 196 (M^+). The ^1H NMR spectrum of this mixture showed δ 9.90 (1 H, d, *J* 2.3), 7.11–7.48 (20 H, m), 4.88 (1 H, d, *J* 2.2) and 4.23 (2 H, s).

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