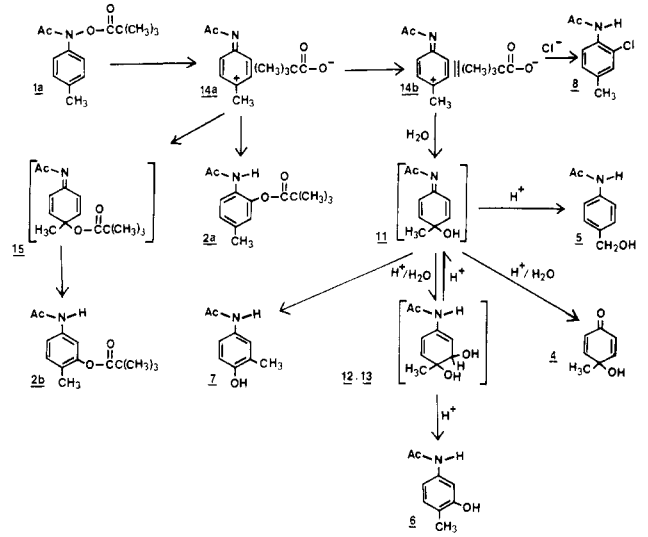
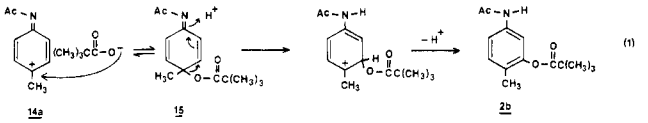
Scheme I

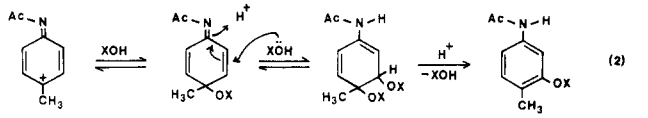


appears to be the most reasonable explanation for the formation of **2b**. The decreased yield of **2b** at higher pH



(1)

can be explained if the 1,2-migration is an acid-catalyzed process. Meta-substitution products have been reported previously to result from the reactions of certain nucleophiles with *N*-acetoxy-*N*-acetyl-2-aminofluorene.[8] Results obtained by Gassman and Granrud[4b] and ourselves[3b] indicated that such products were obtained by an addition–elimination sequence, as in eq 2. However, the ob-



(2)

servation of **2b** in the present study suggests that an alternative process, favored by others,[8b] which involves a 1,2-migration, as in eq 1, is also possible. In any case, the mechanism of eq 2 cannot explain the formation of significant amounts of **2b** because the concentration of free pivalic acid present during the hydrolysis reaction is always considerably less than 1 mM, so that it cannot compete effectively with other nucleophiles present in solution.

Acetanilides are formed when *N*-(sulfonatooxy)acetanilides undergo hydrolysis in the presence of reducing agents.[3] However, the hydrolysis of the *N*-(sulfonatooxy)acetanilides in ordinary phosphate buffer does not yield these products. The 4-acetotoluidide (**9**) isolated during the hydrolysis of **1a** in phosphate buffers is, therefore, an unusual product. The HPLC data taken at pH 7.8 indicate that the formation of **9** is coupled to a decreased yield of at least one of the products **4**, **5**, and **7**.[12] At the present time we do not have sufficient data to speculate intelligently about the mechanism of formation of **9** under these conditions.

Scheme I presents a mechanistic interpretation consistent with the observations made during the hydrolysis reactions of **1a**. With the exception of the path leading to **2b**, Scheme I is essentially identical with that presented earlier to explain the hydrolysis reactions of **1b**.[3b] No pathway leading to **9** is included since we currently do not have an adequate explanation for its origin. The decomposition of **2a** into **3** and **10** has been left out for the sake of clarity. We have no evidence that requires internal return of the tight ion pair, **14a**, to **1a**, although internal return with rearrangement to form **2a** and **2b** does occur. In fact, the formation of the tight ion pair may be the rate-determining step of the reaction.

Acknowledgment. The high-pressure liquid chromatograph used in this study was purchased with funds obtained from the Cotrell Research Grant Program of the Research Corporation. We are also grateful for grant support provided by the American Cancer Society (BC-348).

Registry No. **1a**, 88867-64-5; **1b**, 91631-50-4; **2a**, 98922-96-4; **2b**, 98922-97-5; **3**, 13429-10-2; **4**, 23438-23-5; **6**, 5307-07-3; **7**, 16375-90-9; **10**, 98922-98-6.

Highly Efficient NaOCl Olefin Epoxidations Catalyzed by Imidazole or Pyridine "Tailed" Manganese Porphyrins under Two-Phase Conditions. Influence of pH and of the Anchored Axial Ligand

Fernando Montanari,* Michele Penso, Silvio Quici, and Patrizia Viganò

Centro CNR and Dipartimento di Chimica Organica e Industriale dell'Università, 20133 Milano, Italy

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Mn(III) tetraarylporphyrins **2** and **3**, bearing a pyridine or an *N*-alkyl-substituted imidazole function anchored by an aliphatic chain, are extremely efficient catalysts for olefin epoxidations carried out with NaOCl under aqueous–organic two-phase conditions. Reaction rates are strongly increased by lowering the pH of the aqueous phase, and at pH 9.5 catalyst turnovers are in the range of 0.8–3.3 per s at 0 °C. At the lower pH values rates are only slightly affected by the presence of a phase-transfer catalyst, whereas the latter becomes important at the pH of commercial bleach (12.5–13.0). A similar behavior has been found for epoxidations catalyzed by Mn(III) tetraphenylporphyrin **1**, carried out in the presence of a molar excess of 3-pycoline or *N*-hexylimidazole. The latter is a particularly efficient axial ligand.

Synthetic metalloporphyrins are efficient models of the cytochrome P-450 family of monooxygenase enzymes and have been largely used as catalysts in oxidations of organic substrates.[1] The discovery that manganese(III) tetra-

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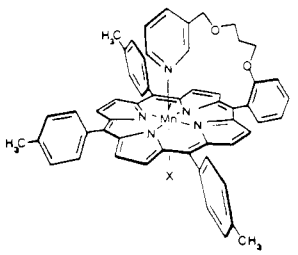
Table I. Oxidations with NaOCl at pH 12.7 under Phase-Transfer Conditions[a]

no.	porphyrin[b]	olefin	organic base	conversn (%)	selectvty (%)	time (min)
1	2	cyclooctene		83.6	100	240
2	3	cyclooctene		93.3	100	240
3	1	cyclooctene	9[c]	100	96.6	120
4	1	cyclooctene	10[d]	94.8	100	30
5	2	*cis*-stilbene		43.3	56.6	30
6	3	*cis*-stilbene		99.8	65.0	30

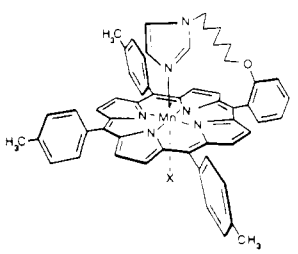
[a] At 25 °C in CH_2Cl_2–H_2O in the presence of 0.012 molar equiv of Aliquat 336 (see Experimental Section). [b] 0.005 molar equiv. [c] 3.0 molar equv. [d] 0.125 molar equiv.

arylporphyrins, like Mn-TPP 1, catalyze the epoxidation of olefins by NaOCl under phase-transfer conditions[2] has aroused particular interest. Reaction rates are increased by addition of a molar excess of pyridines[2,3] or *N*-aryl-substituted imidazoles,[4] which behave as axial ligands on the complexed metal.

We have found that very efficient epoxidation catalysts are easily obtained when a pyridine function or a *N*-alkyl-substituted imidazole is anchored to the porphyrin ring by an aliphatic chain (catalysts **2** and **3**).



2

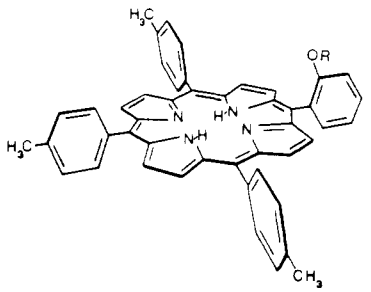


3

Under aqueous–organic two-phase conditions, reaction rates become extremely fast provided that the pH of the aqueous NaOCl is lowered from 12.7 to about 9.5. No extra organic base is required, and rates are only slightly affected by the presence of a phase-transfer catalyst.

Results

Synthesis of Catalysts 2 and 3. Condensation of 5-(2-hydroxyphenyl)-10,15,20-tri-*p*-tolylporphyrin (**4**)[5] with

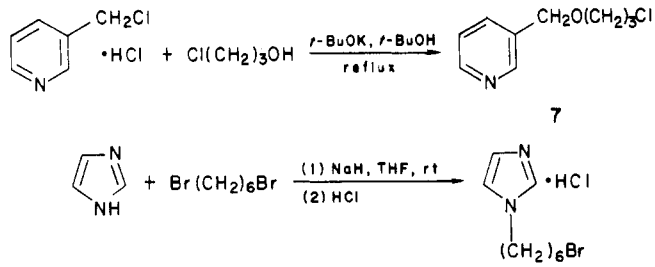


4 R = H

5 R = $(CH_2)_3OCH_2$–(3-pyridyl)

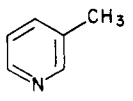
6 R = $(CH_2)_6$–(1-imidazolyl)

pyridine derivative **7** and imidazole derivative **8** (DMF, K_2CO_3, 48 h, room temperature) afforded "tailed" porphyrins **5** and **6** in 85% and 60% yield, respectively. Pyridine derivative **7** was synthesized from 3-(chloromethyl)pyridine hydrochloride and 3-chloropropanol (*t*-BuOH, *t*-BuOK, reflux, 48 h, 42% yield). Reaction of imidazole with excess 1,6-dibromohexane (THF, NaH, room temperature, 24 h, 59% yield) afforded the imidazole derivative, isolated as hydrochloride **8**. The manganese-

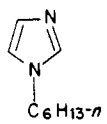


(III) complexes **2** and **3** were prepared from porphyrins **5** and **6** following standard procedures.[6] Both showed Soret bands at 475 nm (CH_2Cl_2).

Olefin Epoxidations. Olefin epoxidations were first carried out in CH_2Cl_2–H_2O with 3.5 molar equiv of 0.35 M NaOCl, 0.005 molar equiv of Mn(III) porphyrin **2** or **3**, 0.012 molar equiv of a phase-transfer catalyst (Aliquat 336) at 25 °C, and the pH of commercial bleach (12.7). As a comparison, reactions were repeated with Mn(III)-TPP **1** in the presence of a molar excess of 3-pycoline (**9**) or *N*-hexylimidazole (**10**) as axial ligands (600 and 25 mol per mol of porphyrin **1**, respectively).[7]



9



10

Good conversions were generally observed in 30–240 min (Table I). Results obtained with **1** in the presence of 3-pycoline were similar to those reported by other authors[2,3] for NaOCl epoxidations carried out under similar conditions. *N*-Hexylimidazole (**10**) appeared to be a particularly efficient axial base. "Tailed" porphyrins **2** and **3** afforded satisfactory results with lower reaction rates

(1) (a) Baldwin, J. E.; Perlmutter, P. *Top. Curr. Chem.* **1984**, *121*, 181–220. (b) Meunier, B. *Bull. Soc. Chim. Fr.* **1983**, 345–366.

(2) (a) Meunier, B.; Guilmet, E.; De Carvalho, M. E.; Poilblanc, R. *J. Am. Chem. Soc.* **1984**, *106*, 6668–6676, and references therein. (b) Bartolini, O.; Meunier, B. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1967–1970. (c) De Poorter, B.; Meunier, B. *Tetrahedron Lett.* **1984**, *25*, 1895–1896. (d) Bartolini, O.; Momenteau, M.; Meunier, B. *Tetrahedron Lett.* **1984**, *25*, 5773–5776. (e) Collmann, J. P.; Brauman, J. I.; Meunier, B.; Hayashi, T.; Kodadek, T.; Raybuck, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 2000–2005, and references therein.

(3) Razenberg, J. A. S. J.; Nolte, R. J. M.; Drenth, W. *Tetrahedron Lett.* **1984**, *25*, 789–792.

(4) Collmann, J. .; Kodadek, T.; Raybuch, S. A.; Meunier, B. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7039–7041.

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(6) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443–2445.

(7) Higher amounts of *N*-hexylimidazole (>40 molar equiv per mol of 1) led to fast degradation of the porphyrin. On the contrary, in the case of pyridine bases it was demonstrated[3] that epoxidation rates of cyclohexene catalyzed by 1 increase with increasing concentration of base up to a maximum ratio base/Mn-TPP of 650, and subsequently they slow down to zero.

Table II. Influence of pH and of Phase-Transfer Catalyst (PT) on the Epoxidation of Cyclooctene with "Tailed" Porphyrins 2 and 3[a]

no.	porphyrin[b]	PT[c]	pH	temp (°C)	conversn (%)	selectvty (%)	time[d] (min)
1	2	PT	12.7	25	68.5	100	120
2			12.7	25	21.8	87.6	120
3		PT	12.0	25	50.5	98.7	90
4			12.0	25	37.5	90.6	90
5		PT	11.0	25	64.7	99.9	10
6			11.0	25	77.8	96.4	10
7		PT	9.5	0	95	96.2	4 (≤8)
8			9.5	0	95	97.2	9 (12)
9	3	PT	12.7	25	70	99	120
10			12.7	25	20	72.2	120
11		PT	9.5	0	95	93.5	5 (10)
12			9.5	0	95	94.0	11 (15)

[a] In CH_2Cl_2–H_2O. [b] 0.005 molar equiv. [c] 0.012 molar equiv. [d] In parentheses: time required for 100% conversion.

Table III. Olefin Epoxidations at pH 9.5 and 0 °C with Porphyrins 2 and 3[a]

no.	porphyrin	olefin	conversn[b] (%)	selectvty (%)	time (min)	rate[c] (turnovers per s)
1	2	cyclooctene	95	96.2	4	2.7
2	3		95	93.5	5	2.7
3	2	*cis*-stilbene	95	66.5	1	3.0
4	2		100[d]	70.9	8	0.8
5	3		100	81.0	≤1	3.3
6	3		100[d]	71.4	≤3	1.1
7	2	*trans*-stilbene	26	100	1	
8	2[e]		94.4	82.6	8	
9	3		23.1	100	1	
10	2	styrene	95.5[d]	61.4	6	1.4
11	3		91.3[d]	62.0	5	1.5
12	2	2-methyl-2-heptene	97.9[d]	96.2	5	2.8
13	3		97.4[d]	95.4	10	2.7

[a] In CH_2Cl_2–H_2O, with 0.005 molar equiv of 2 or 3 and 0.012 molar equiv of Aliquat 336. [b] With the only exception of *trans*-stilbene, all oxidations reached 100% conversion. [c] mmol of olefin consumed per mmol of porphyrin per s at 40–50% conversions. [d] No phase-transfer catalyst. [e] 0.025 molar equiv, at 25 °C.

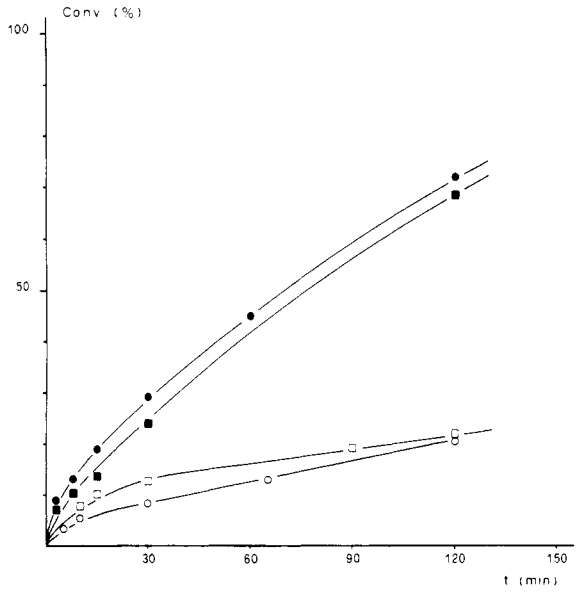


Figure 1. Influence of phase-transfer catalyst on the oxidation of cyclooctene catalyzed by "tailed" porphyrins 2 (■, □) and 3 (●, ○) at pH 12.7 and 25 °C. Presence (full symbols) and absence (empty symbols) of phase-transfer catalyst.

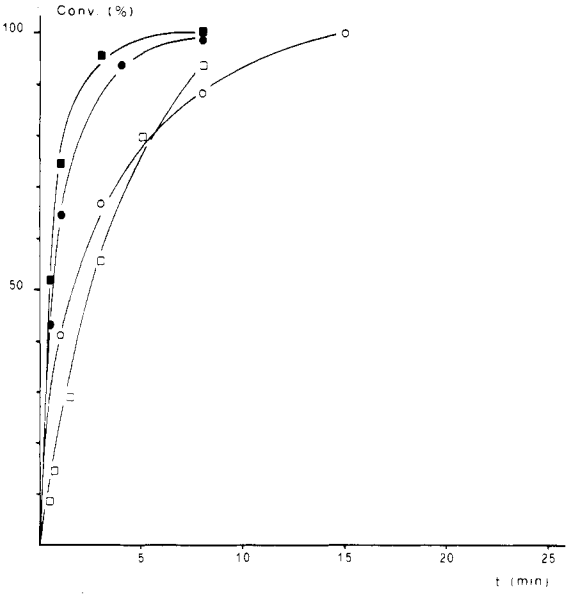


Figure 2. Influence of phase-transfer catalyst on the oxidation of cyclooctene catalyzed by porphyrins 2 (■, □) and 3 (●, ○) at pH 9.5 and 0 °C. Presence (full symbols) and absence (empty symbols) of phase-transfer catalyst.

without requiring any added base. Selectivities were very high for cyclooctene, lower for, *cis*-stilbene.

As shown in Table II and in Figures 1 and 2 for the oxidation of cyclooctene catalyzed by "tailed" porphyrin 2, reaction rates progressively increased when the pH of the aqueous phase was lowered by addition of HCl. At pH 9.5 epoxidations were almost immediate, and they could be better monitored at 0 °C. Under these conditions conversion of cyclooctene was 95% after 4 min with 96.2 selectivity.[8] At pH 12.7 the addition of a phase-transfer catalyst noticeably affected the reaction rates, expecially

(8) At pH 8.0–9.0, under phase-transfer conditions, HOCl epoxidizes arenes to arene oxides in high yields and alkenes to a complex mixture of chlorinated and oxidized products, including the epoxide. These reactions should proceed by a free-radical mechanism involving Cl_2O and ClO·radical. No reaction occurs at higher pH.[9]

(9) (a) Krishnan, S.; Kuhn, D. G.; Hamilton, G. A. *J. Am. Chem. Soc.* **1977**, *99*, 8121–8123. (b) Fonouni, H. E.; Krishnan, S.; Kuhn, D. G.; Hamilton, G. A. *Ibid.* **1983**, *105*, 7672–7676.

Table IV. Influence of pH, of Phase-Transfer Catalyst (PT), and of the Added Base on the Epoxidation of Cyclooctene with Mn-TPP 1[a]

no.	PT[b]	pH	organic base	temp (°C)	conversn (%)	selectvty (%)	time[c] (min)
1	PT	12.7	**9**[d]	25	95	96.6	100
2		12.7		25	70	98.5	100
3	PT	12.0		25	75.2	100	10 (20)
4		12.0		25	44.8	98.7	10 (40)
5	PT	9.5		25	98.0	87.5	10 (15)
6		9.5		25	77.6	87.4	10 (20)
7	PT	8.5		25	79.9	82.5	5 (≤10)
8		8.5		25	62.8	85.0	5 (≤15)
9	PT	12.7	**10**[e]	25	94.8	100	30
10		12.7		25	56.5	100	30
11	PT	9.5		0	95.6[f]	100	100 (≤15)
12		9.5		0	64[g]	100	100 (≤25)
13	PT	9.5	none	25	48	72	200

[a] 0.05 molar equiv in CH_2Cl_2–H_2O. [b] 0.012 molar equiv. [c] In parentheses: time required for 100% conversion. [d] 3.0 molar equiv. [e] 0.125 molar equiv. [f] 0.5 turnovers per s at 45% conversion. [g] 0.2 turnovers per s at 45% conversion.

at higher conversions (Figure 1), but its influence was very small at lower pH's (Figure 2). The same behavior was shown by porphyrin **3**.

Epoxidation of different olefins at pH 9.5 and 0 °C are reported in Table III. As for cyclooctene, rates were only slightly affected by the addition of a quaternary salt. Oxidation of *cis*-stilbene was almost complete in 1–3 min. In this case selectivities were in the range 66–81%, the other products being essentially *trans*-stilbene oxide and phenyl benzyl ketone, in about a 1:1 ratio. *trans*-Stilbene was selectively oxidized to *trans*-stilbene oxide up to about 25% in 1 min, but at this point the catalyst was completely degraded and the reaction stopped. However, oxidation could be carried out to completion in the presence of 0.025 molar equiv of porphyrin at 25 °C. Styrene and 2-methyl-2-heptene were easily oxidized in a few minutes. Selectivities were very high for 2-methyl-2-heptene, but lower for styrene, mainly due to the formation of 2-phenylacetaldehyde.[10]

As shown in Figure 2 an almost linear percent conversion vs. time relationship was observed at low pH's and at early reaction times. Then, a progressive degradation of porphyrin occurred, and the organic solution was totally bleached in a few minutes after all the olefin was converted.

A dramatic increase of reaction rates on diminishing the pH of the aqueous phase was also observed in the oxidations catalyzed by Mn-TPP **1** in the presence of 3-pycoline (**9**) or *N*-hexylimidazole (**10**) (Table IV and Figure 3). With **9** (600 mol per mol of **1**) conversion of cyclooctene was complete in 20 min at pH 12.0 and in 15 and 10 min at pH 9.5 and 8.5, respectively. However, selectivities were also noticeably lowered and reached 82.5% at pH 8.5. *trans*-1,2-Dichlorocyclooctane was the only observed side product.[11]

At the lower pH values, rates were only slightly affected by the addition of a quaternary salt, but the latter became important at pH 12.7. With Mn-TPP **1** and *N*-hexylimidazole (**10**) (25 mol/mol of **1**), oxidation of cyclooctene was almost immediate at pH 9.5 and 25 °C. At 0 °C in the presence of a quaternary salt, it was complete in 15 min and without the salt in 25 min.[13]

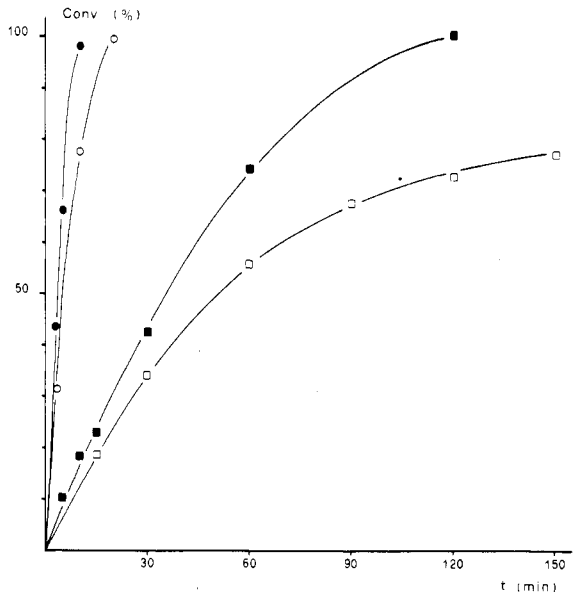


Figure 3. Influence of pH on the oxidation of cyclooctene catalyzed by porphyrin **1** and **9**, as extra base, at 25 °C (pH 9.5 (●, ○), pH 12.7 (■, □)). Presence (full symbols) and absence (empty symbols) of phase-transfer catalyst.

Discussion and Conclusions

Syntheses of porphyrins in which the axial substituent is appended by a "tail" connected to the porphyrin ring have been reported by several authors.[1a,15] It has been recently published[2d] that the manganese(III) complex of a bridged porphyrin **11** bearing a pyridine function is a better epoxidation catalyst than **1**, when used without extra pyridine. However, **1** remains a more efficient cat-

(10) Relatively low selectivities are generally found in porphyrin-catalyzed oxidations of *cis*-stilbene and styrene.[2,12]

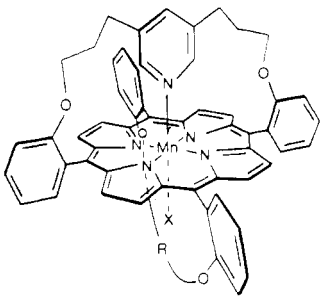
(11) Small amounts of other unidentified impurities were slowly formed after conversion was complete. Furthermore, the initial low pH's rapidly increased to almost 11.5 during the reaction.

(12) (a) Groves, J. T.; Kruper, W. J.; Haushalter, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6375–6377. (b) Guilmet, E.; Meunier, B. *Nouv. J. Chim.* **1982**, *6*, 511–513. (c) Murugesan, N.; Hecht, S. M. *J. Am. Chem. Soc.* **1985**, *107*, 493–500.

(13) It has been reported[4,14] that 4'-(imidazol-1-yl)acetophenone is a more efficient axial base than 3-phenylpyridine, a behavior which parallels that of *N*-hexylimidazole (**10**) and 3-pycoline (**9**). It has been also reported[2] that *N*-methylimidazole does not work as an axial base in the presence of Mn-TPP **1**. It seems possible that this inefficiency depends on its high solubility in water, whereas **10** is practically insoluble in the latter.

(14) Collman, J. P.; Brauman, J. I.; Meunier, B.; Raybuck, S. A.; Kodadek, T. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 3245–3248.

(15) (a) Collman, J. P.; Brauman, J. I.; Doxsee, K. M.; Halbert, T. R.; Bunnenberg, E.; Linder, R. E.; La Mar, G. N.; Del Gaudio, J.; Lang, G.; Spartalian, K. *J. Am. Chem. Soc.* **1980**, *102*, 4182–4192. (b) Walker, F. A.; Benson, M. *J. Am. Chem. Soc.* **1980**, *102*, 5530–5538. (c) Gunter, M. J.; Mander, L. N. *J. Org. Chem.* **1981**, *46*, 4792–4795. (d) Momenteau, M.; Lavalette, D. *J. Chem. Soc., Chem. Commun.* **1982**, 341–343. (e) Momenteau, M.; Loock, B.; Lavalette, D.; Tétreau, C.; Mispelter, J. *J. Chem. Soc., Chem. Commun.* **1983**, 962–964. (f) Saxton, R. J.; Wilson, L. J. *J. Chem. Soc., Chem. Commun.* **1984**, 359–361. (g) Momenteau, M.; Mispelter, J.; Loock, B.; Lhoste, J.-M. *J. Chem. Soc., Perkin Trans. 1* **1985**, 221–231.



11 R = $(CH_2)_{12}$, $(CH_2)_4C_6H_4(CH_2)_4$

alyst than 11 when it is used in the presence of an excess of extra pyridine.

Differently from most of the "tailed" porphyrins reported up to now, porphyrins **2** and **3** have the advantage of requiring a relatively easy synthesis. The pyridine or imidazole functions, although appended to the porphyrin ring with a single arm, behave as very efficient axial ligands at the optimum pH conditions.

As shown above, addition of a phase-transfer catalyst to the two-phase system is not necessary for reactions carried out at pH's ≤12.0. Despite what has been reported up to now,[2-4,14] a phase-transfer catalyst is not strictly necessary even at pH 12.7. Indeed, HOCl is a very weak acid (pK_a = 7.54),[16] so that the anion and the undissociated species coexist in a wide pH range. Hypochlorous acid is largely soluble in polar organic solvents,[16] and it is extracted from the aqueous phase into CH_2Cl_2. As shown in Table V, expecially at lower pH's, molarities of HOCl in the CH_2Cl_2 solution measured under reaction conditions, are comparable with, or higher than, those of porphyrins **1–3** and of quaternary ammonium cation (0.2×10^{-2} and 0.48×10^{-2} M, respectively). The latter represent the maximum amount of ClO^- possibly present in the organic phase under phase-transfer conditions.

To the best of our knowledge, olefin epoxidations catalyzed by "tailed" porphyrins **2** and **3** at pH 9.5 are among the fastest reported up to now. Reaction rates, calculated as turnovers of catalysts per s at the early reaction times (40–50% conversions), are in the range 0.8–3.3 at °C (Table III), whereas under the same conditions, oxidations of cyclooctene catalyzed by Mn-TPP **1** in the presence of 25 molar equiv of **10** per mol of porphyrin proceed at 0.2–0.5 turnovers per s (Table IV). Maximum ranges of 100–750 turnovers per h[4] and 4–11 turnovers per s[2e] at room temperature have been reported for reactions carried out with Mn-porphyrins and an excess of added pyridine and imidazole ligand, respectively.

In the absence of extra ligand, Mn-TPP **1** displays a very low efficiency even at pH 9.5 (Table IV), as demonstrated by other authors[2a] for reactions carried out at pH of the commercial bleach.

It has been recently demonstrated[2e,14] that in the hypochlorite epoxidation of olefins catalyzed by Mn(III) porphyrins under phase-transfer conditions reaction occurs via an oxo–olefin intermediate **14**, which derives from hypochlorite adduct **12**, and whose breakdown to form epoxide and Mn porphyrin **15** is the rate-determining step of the catalytic cycle (Scheme I). Both formation of this intermediate and its subsequent breakdown are, in general, concerted processes.

We can speculate that a similar mechanism applies at lower pH's of the aqueous phase, and the breakdown of intermediate **14** is speeded up by the HOCl species present in the organic phase. Current investigations will provide deeper insight on the mechanistic aspects on this reaction.

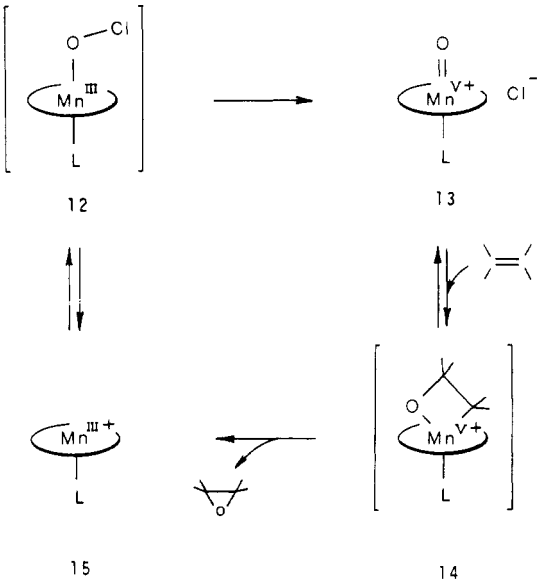
(16) Kirk-Othmer; "Encyclopedia of Chemical Technology", 3rd ed.; John Wiley and Sons; New York; 1979; Vol. 5, pp 585–611.

Table V. Molarity of HOCl in the CH_2Cl_2 Solution[a]

pH	HOCl, M × 10^2	
	no added base	with 3-pycoline[b]
9.5[c]	0.85	1.20
12.0	0.05	0.20
12.7	0.04	0.07

[a] After equilibration at 25 °C with 0.35 M aqueous NaOCl under the reaction conditions, but in the absence of substrate and of porphyrin. [b] 1.20 M. [c] In the presence of 3-pycoline, initial value.

Scheme I



Experimental Section

General Methods. ^1H NMR spectra were recorded on a Bruker WP 80 SY spectrometer with Me_4Si as an internal standard. Infrared and UV spectra were obtained with a Perkin-Elmer 377 spectrometer and with a Varian-Cary 219 spectrophotometer, respectively. GLC analyses were performed on a Varian Model 3700 gas chromatograph Vista CDS 401 Chromatography Data System flame ionization instrument (20 ft × 0.125 in. OV-101-5% on CHP 100–125 mesh and 5 ft × 0.25 in. Carbovax 20M-3% in DMCS 100–125 mesh columns). Satisfactory combustion analyses were obtained ($C = \pm 0.40$, $H = \pm 0.20$, $N = \pm 0.20$) for all new compounds. Organic and inorganic reagents, ACS grade, were used without further purification.

trans- and *cis*-Stilbene oxide,[17] 2,3-epoxy-3-methylheptene,[18] styrene oxide,[17] cyclooctene oxide,[17] *trans*-1,2-dichlorocyclooctane,[19] and phenyl acetaldehyde,[17] as reference compounds, and 5-(2-hydroxyphenyl)-10,15,20-tri-*p*-tolylporphyrin[5] (**4**) were prepared following standard procedures.

***N*-(6-Bromohexyl)imidazole Hydrochloride (8).** A solution of imidazole (1.94 g, 30 mmol) in 80 mL of anhydrous THF was added to a stirred suspension of 80% NaH mineral oil (0.90 g, 30 mmol) in 20 mL of THF at room temperature. The mixture was stirred for 1 h, and then 1,6-dibromohexane (22 g, 90 mmol) was added. The reaction mixture was stirred overnight at room temperature. The solid was filtered off and washed with ethyl ether (2 × 20 mL), and the solvent was evaporated in vacuo at 30 °C. The residue was dissolved in ethyl ether (200 mL), washed with water (3 × 30 mL), dried over Na_2SO_4, and concentrated to 70 mL, and the solution was purified by column chromatography

(17) "Dictionary of Organic Compounds", 5th ed.; Bukingam, J., Ed.; Chapman and Hall: New York, 1982.
(18) Cornforth, J. W.; Cornforth, R. H.; Mathew, K. K. *J. Chem. Soc.* **1959**, *81*, 112–127.
(19) Kohler, E. P.; Tishler, M.; Potter, H.; Thompson, H. T. *J. Am. Chem. Soc.* **1939**, *61*, 1057–1061.

(silica gel, ethyl ether–THF). The eluate was saturated with anhydrous HCl and evaporated to afford 4.71 g (59%) of a thick hygroscopic oil: ^{1}H NMR ($CDCl_3$) δ 1.20–2.20 (m, 8 H), 3.40 (t, 2 H), 4.35 (t, 2 H), 7.20 (s, 1 H), 7.45 (s, 1 H), 9.6 (s, 1 H), 12.0 (br s, 1 H, D_2O exchange).

***N*-Hexylimidazole (10).** A solution of imidazole (6.8 g, 0.1 mol) in 80 mL of anhydrous THF was added to a stirred suspension of 80% NaH mineral oil (3.6 g, 0.12 mol) in 50 mL of THF at room temperature. The mixture was stirred for 1 h and then a solution of 1-bromohexane (16.5 g, 0.1 mol) and tetrabutylammonium hydrogen sulfate (1.7 g, 5 mmol) in 50 mL of THF was added. After 15 h at room temperature, the precipitate was filtered and washed with CH_2Cl_2 (2 × 30 mL); evaporation of the solvent gave 18.2 g of an oil. Column chromatography (silica gel, ethyl acetate) afforded 14.8 g (97%) of **10** as a colorless oil: n^{20}_D = 1.4760; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3 H), 1.10–2.10 (m, 8 H), 3.95 (t, 3 H), 6.8 (s, 1 H), 6.95 (s, 1 H), 7.35 (s, 1 H).

3-[(3-Chloropropoxy)methyl]pyridine (7). 3-Chloropropanol (1.0 g, 10.6 mmol) was stirred at room temperature for 1 h with a solution of potassium *tert*-butoxide (3.63 g, 31.8 mmol) in 75 mL of THF, and after this time 3-(chloromethyl)pyridine hydrochloride (1.74 g, 10.6 mmol) was added. The reaction mixture was stirred at room temperature for 48 h and then refluxed for an additional 20 h. After filtration and evaporation of the solvent in vacuo, the residue was dissolved in 100 mL of ethyl acetate, washed with water (2 × 50 mL), dried over $MgSO_4$, and evaporated. Column chromatography (silica gel, ethyl acetate) afforded 0.83 g (42.2%) of **7** as an oily product: ^{1}H NMR ($CDCl_3$) δ 1.70–2.20 (m, 2 H), 3.30–3.70 (m, 4 H), 4.45 (t, 2 H), 7.05–7.25 (m, 1 H), 7.50–7.70 (m, 1 H), 8.40–8.65 (m, 2 H).

5-[2-[3-(Pyrid-3-ylmethoxy)propoxy]phenyl]-10,15,20-tri-*p*-tolylporphyrin (5). A solution of porphyrin **4** (0.25 g, 0.37 mmol) and 3-[(3-chloropropoxy)methyl]pyridine (0.08 g, 0.41 mmol) in 7.5 mL of DMF was stirred at room temperature for 16 h in the presence of K_2CO_3 (0.75 g, 5.43 mmol). After evaporation of the solvent, the residue was dissolved in 25 mL of ethyl acetate, washed with water (2 × 20 mL), dried over Na_2SO_4, and evaporated. Column chromatography (silica gel, ethyl acetate) afforded 0.26 g (85%) of **5** as a purple powder: ^{1}H NMR ($CDCl_3$) δ −2.80 (s, 2 H), 1.20 (m, 2 H), 2.15 (t, 2 H), 2.60 (s, 9 H), 3.20 (s, 2 H), 3.95 (t, 2 H), 7.15–8.30 (m, 20 H), 8.80 (d, 8 H); λ_{max} (ϵ/mmol L^{-1}) (CH_2Cl_2), 516 (19.9), 550 (8.7), 589 (5.9), and 645 nm (4.4).

5-[2-[3-(Pyrid-3-ylmethoxy)propoxy]phenyl]-10,15,20-tri-*p*-tolylporphyrin Mn(III) Acetate Complex (2). A solution of 0.100 g (0.122 mmol) of porphyrin **5** and 0.066 g (0.269 mmol) of $Mn(OAc)_2{\cdot}4H_2O$ in 20 mL of DMF was stirred and refluxed for 2 h. After evaporation of the solvent under vacuum, the residue was dissolved in 20 mL of CH_2Cl_2, washed with water (2 × 20 mL), dried over Na_2SO_4, and evaporated; crystallization with CH_2Cl_2/*n*-Pentane afforded 0.103 g (90%) of a **2** as a green solid: λ_{max} (ϵ/mmol L^{-1}) (CH_2Cl_2) 475 (87.1), 524 (5.4), 580 (8.4), and 618 nm (8.6).

5-[2-[[6-(*N*-Imidazolyl)hexyl]oxy]phenyl]-10,15,20-tri-*p*-tolylporphyrin (6). A solution of porphyrin **4** (0.395 g, 0.59 mmol) and *N*-(6-bromohexyl)imidazole hydrochloride (0.63 g, 2.34 mmol) in 12 mL of DMF was stirred at room temperature for 48 h in the presence of K_2CO_3 (2.37 g, 17.1 mmol). After evaporation of the solvent, the residue was dissolved in 150 mL of CH_2Cl_2, washed with water (2 × 50 mL), dried over Na_2SO_4, and evaporated. Column chromatography (silica gel, ethyl acetate) afforded 0.276 g (57%) of **6** as a purple powder: ^{1}H NMR ($CDCl_3$) δ −2.60 (s, 2 H), 0.0–0.46 (m, 6 H), 0.95 (t, 2 H), 2.0 (t, 2 H), 2.70 (s, 9 H), 3.82 (t, 2 H), 6.50 (d, 2 H), 7.23 (s, 1 H), 7.34–8.25 (m, 16 H), 8.81 (d, 8 H); λ_{max} (ϵ/mmol L^{-1}) (CH_2Cl_2) 516 (16.0), 551 (7.5), 590 (4.8), and 647 nm (4.1).

5-[2-[[6-(*N*-Imidazolyl)hexyl]oxy]phenyl]-10,15,20-tri-*p*-tolylporphyrin Mn(III) Acetate Complex (3). A solution of 0.119 g (0.145 mmol) of porphyrin **6** and 0.071 g (0.290 mmol) of $Mn(OAc)_2{\cdot}4H_2O$ in 20 mL of DMF was stirred and refluxed for 2 h. After evaporation of the solvent under vacuum, the residue was dissolved in 20 mL of CH_2Cl_2, washed with water (2 × 20 mL), dried over Na_2SO_4, and evaporated. Crystallization with CH_2Cl_2/*n*-pentane afforded 0.120 g (89%) of **3** as a green solid: λ_{max} (ϵ/mmol L^{-1}) (CH_2Cl_2) 475 (96.2), 525 (5.2), 576 (8.0), and 613 nm (8.9).

Titration of HOCl Extracted by CH_2Cl_2. A 50-mL flask equipped with a Teflon-lined screw cap and magnetic stirrer, thermostated at 25 °C (as above), was charged with 32 mL of aqueous 0.35 M NaOCl at the appropriate pH, 8 mL of CH_2Cl_2, and 0.94 mL of 3-pycoline (**9**) (when present). The mixture was stirred for 30 min and then let stand for 5 min to allow separation of the phases. Aliquots (3 mL) of the organic solution were withdrawn and stirred with 20 mL of aqueous 10% KI and 1 mL of concentrated aqueous HCl for 20 min and then titrated with 0.01 N-$Na_2S_2O_3$ aqueous solution, with 1% aqueous solution of starch as indicator. Results are reported in Table V and are the average of at least two measurements.

General Procedure of Olefin Epoxidation. Oxidations were run in a 20-mL flask equipped with a Teflon-lined screw cap thermostated at the appropriate temperature with circulating water or ethanol and magnetic stirrer. The temperature was controlled at 25 ± 0.01 °C by a Exacal 200 Bath Circulator and 0 ± 0.2 °C by a Colora Misstechnik GMBH Lorch/Württ Cryostat. Stirring speed was maintained at 1300 ± 50 rpm. The flask was charged with 1 mL of CH_2Cl_2 solution, containing 0.8 mmol of substrate, 0.96 × 10^{-2} mmol of Aliquat (when used), and 0.24 mmol of decane, dodecane, or tetradecane as the internal standard, 1 mL of 0.4 × 10^{-2} M CH_2Cl_2 solution of porphyrin, and 8 mL of aqueous 0.35 M NaOCl. The pH of this solution was first brought to the desired value by adding 10% HCl aqueous solution. When the Mn(III)-TPP **1** was the catalyst, the required amount of extra organic base **9** (2.4 mmol) or **10** (0.1 mmol) was added via syringe. The mixture was stirred, and samples withdrawn at different times were analyzed by GLC.

Registry No. **2** (X = acetate), 98875-81-1; **3** (X = acetate), 98875-82-2; **4**, 57412-07-4; **5**, 98875-79-7; **6**, 98875-80-0; **7**, 98875-78-6; **8**, 98875-77-5; **9**, 108-99-6; **10**, 33529-01-0; NaOCl, 7681-52-9; imidazole, 288-32-4; 1,6-dibromohexane, 629-03-8; 1-bromohexane, 111-25-1; 3-chloropropanol, 627-30-5; 3-(chloromethyl)pyridine hydrochloride, 6959-48-4; cyclooctene, 931-88-4; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; styrene, 100-42-5; 2-methyl-2-heptene, 627-97-4.