

## Epoxidation Catalysed by $Mn^{III}TPPCL$ using Dioxygen Activated by a System Containing *N*-Hydroxyphthalimide and Styrene, 2-Norbornene or Indene

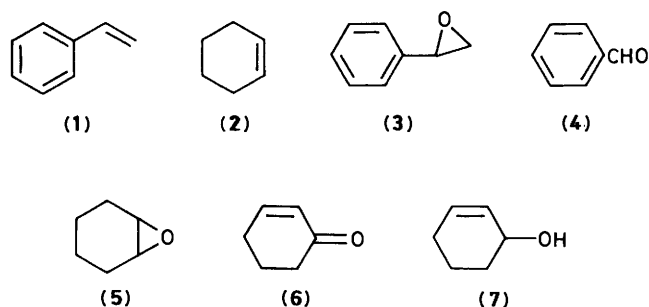
Shigeko Ozaki,\* Tomomi Hamaguchi, Keiichi Tsuchida, Yukio Kimata, and Masaichiro Masui  
Faculty of Pharmaceutical Sciences, Osaka University 6-1 Yamadaoka Suita, Osaka-fu, 565 Japan

The catalytic epoxidation of alkenes by molecular oxygen activated in the system containing *N*-hydroxyphthalimide (NHPI) and active alkenes such as styrene, 2-norbornene or indene is reported. The transient intermediates, alkyl hydroperoxides formed by autoxidation of NHPI and the active alkenes are proposed as oxygen sources which transfer mono-oxygen to  $Mn^{III}TPPCL$ .

In order to clarify the structural characteristics of the active species involved in reactions of cytochrome P-450, a typical mono-oxygenase, many systems have been investigated.<sup>1</sup> Among those model systems, the mechanism whereby dioxygen is activated by the reducing agents such as  $H_2$ /colloidal Pt,  $NaBH_4$ ,<sup>2a-f</sup> or zinc amalgam<sup>2g</sup> in the presence of metalloporphyrin, and where molecular oxygen,  $O_2$ , is activated electrochemically at a glassy carbon electrode<sup>2h</sup> or by an acylating agent,<sup>2i</sup> have attracted much attention lately.

We have previously reported the catalytic epoxidation of alkenes by  $O_2$  activated by the system containing styrene, *N*-hydroxyphthalimide (NHPI), pyridine, and  $Mn^{III}TPPCL$ ,<sup>3</sup> where epoxidation of styrene itself and of added alkenes took place stereospecifically [(*Z*)- and (*E*)-stilbene].

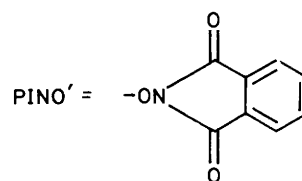
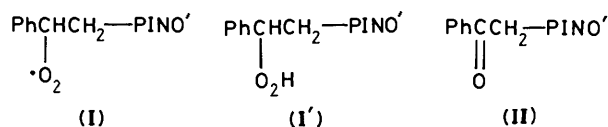
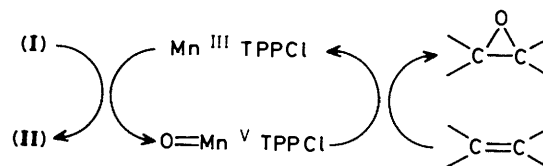
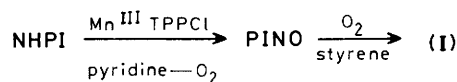
The good turnover numbers of the catalyst reflected in the yields of styrene oxide and cyclohexene oxide indicate that  $Mn^{III}TPPCL$  acts as a real catalyst for the epoxidation. In the case of alkenes bearing allylic hydrogens such as cyclohexene, the corresponding enone was formed in a larger yield than the epoxide. As shown by the results of runs 3 and 4, cyclohexene oxide (5), cyclohex-2-enone (6), and cyclohex-2-enol (7) were



also formed, probably by  $Mn^{III}TPPCL$ -catalysed autoxidation<sup>4</sup> (run 3) or by the autoxidation induced by phthalimide *N*-oxyl (PINO') which was prepared electrochemically<sup>5</sup> (run 4). The product distribution of these three compounds is, however, quite different from that of run 2. Thus, in the epoxidation of alkenes by the present system, both the catalytic epoxidation by activated  $O_2$ , and a radical, PINO, induced autoxidation of alkenes seem to take place at the same time.

In the previous paper, we tentatively proposed the reaction route depicted in Scheme 1 for the epoxidation by the present system.

As mentioned in the previous paper, the direct observation



Scheme 1.

of the presumed intermediate, high-valent oxo-manganese complex  $O=Mn^VTPPCL$  is impossible in our system, since it is only attainable in the presence of an excess of styrene, which must react with  $O=Mn^VTPPCL$  instantaneously (see the Experimental). We identified only the carbonyl compound (II) (Scheme 1) as the compound which resulted from the reaction of  $O=Mn^VTPPCL$  and another presumed intermediate, the peroxy radical (I') (Scheme 1).

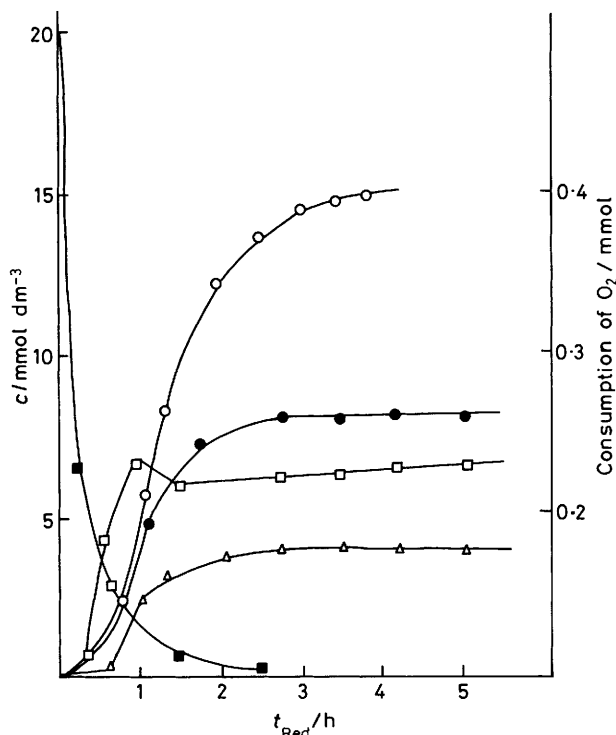
We now report results of further investigations which verify the proposed reaction path by providing further support for the intermediacy of another intermediate, the peroxy radical (I) or the hydroperoxide (I') in the present system. If Scheme 1 is operative in the present system,  $O=Mn^VTPPCL$  would be formed in a yield close to that of the carbonyl compound (II), i.e. in 50% yield, which means at the same time that styrene oxide should also be obtained in a similar yield. The yield of styrene oxide was, however, 27% (run 1). This seems to suggest that

† Tetraphenylporphyrinato manganese(III) chloride.

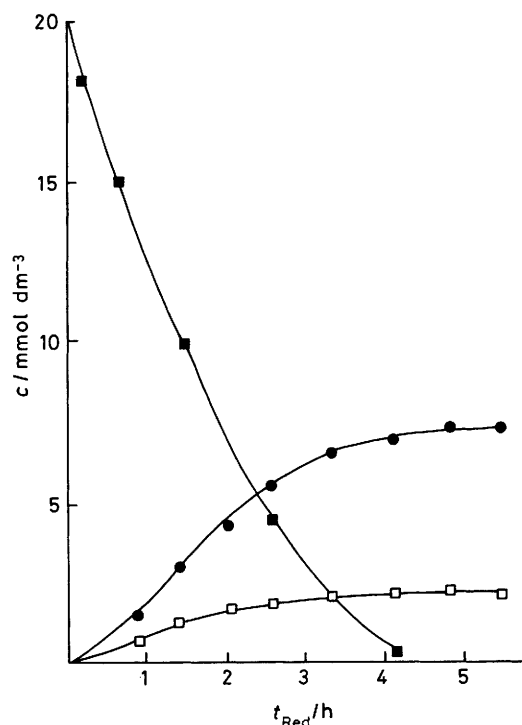
**Table 1.** Oxidation of styrene and cyclohexane catalysed by  $\text{Mn}^{\text{III}}$ -TPPCL.<sup>a</sup>

| Run            | [Alkene]/<br>$\text{mmol dm}^{-3}$ |     | Products yields(%) <sup>b</sup> |     |                            |     |     |
|----------------|------------------------------------|-----|---------------------------------|-----|----------------------------|-----|-----|
|                | (1)                                | (2) | (3)                             | (4) | (5)                        | (6) | (7) |
| 1              | 120                                | 0   | 27<br>(3 860) <sup>c</sup>      | 11  |                            |     |     |
| 2              | 25                                 | 120 | 5                               | 8   | 41<br>(5 860) <sup>c</sup> | 70  | 20  |
| 3              | 0                                  | 120 |                                 |     | 13                         | 180 | 30  |
| 4 <sup>d</sup> | 0                                  | 120 |                                 |     | 6                          | 62  | 10  |

<sup>a</sup> The reaction was performed under a typical conditions, *i.e.*, in acetonitrile ( $20 \text{ cm}^3$ ) containing styrene ( $120$  or  $25 \text{ mmol dm}^{-3}$ ), NHPI ( $20 \text{ mmol dm}^{-3}$ ),  $\text{Mn}^{\text{III}}$ TPPCL ( $0.14 \text{ mmol dm}^{-3}$ ) and pyridine ( $80 \text{ mmol dm}^{-3}$ ) under an atmosphere of air at  $30^\circ\text{C}$ . <sup>b</sup> Yield based on NHPI. <sup>c</sup> Yield based on  $\text{Mn}^{\text{III}}$ TPPCL. <sup>d</sup> Result of anodic oxidation of cyclohexene ( $120 \text{ mmol dm}^{-3}$ ) using NHPI ( $20 \text{ mmol dm}^{-3}$ ) as a mediator at  $0.85 \text{ V vs. SCE}$ .<sup>5</sup>

**Figure 1.** Formation of the carbonyl compound (9) (●), the hydroxide (8) (□), and benzaldehyde (△), consumption of  $\text{O}_2$  (○), and disappearance of NHPI (■) in the oxidation of styrene ( $120 \text{ mmol dm}^{-3}$ ) catalysed by  $\text{Mn}^{\text{III}}$ TPPCL ( $0.14 \text{ mmol dm}^{-3}$ ) in the presence of pyridine ( $80 \text{ mmol dm}^{-3}$ ) in acetonitrile at  $30^\circ\text{C}$ .

there might be other compounds resulting from the peroxy radical (I) or the hydroperoxide (I'). On examination of the reaction products, we found that another product, *N*-(2-hydroxy-2-phenylethoxy)phthalimide [(8), Table 2], the corresponding hydroxide, was formed gradually in up to 33% yield in 3 h, together with the carbonyl compound (II) or (9) (Table 2), styrene oxide (27%), and benzaldehyde (11%). About 60% of the  $\text{Mn}^{\text{III}}$ TPPCL was recovered under the typical experimental conditions using styrene ( $120 \text{ mmol}$ ), NHPI ( $20 \text{ mmol}$ ), pyridine ( $80 \text{ mmol}$ ) and  $\text{Mn}^{\text{III}}$ TPPCL ( $0.14 \text{ mmol}$ ) dissolved in acetonitrile ( $20 \text{ cm}^3$ ) at  $30^\circ\text{C}$ . In Figure 1, the plot of formation of the

**Figure 2.** Formation of the carbonyl compound (9) (●) and the hydroxide (8) (□) and the disappearance of NHPI (■) in the anodic oxidation of NHPI at  $0.85 \text{ V vs. SCE}$  in the presence of styrene ( $120 \text{ mmol dm}^{-3}$ ) and pyridine ( $80 \text{ mmol dm}^{-3}$ ).

hydroxide (8), the carbonyl compound (9), styrene oxide and benzaldehyde, and uptake of  $\text{O}_2$  versus time are shown along with that of consumption of NHPI.

The consumption of NHPI and  $\text{O}_2$  showed variety of induction times, 5–120 min, which disappeared in the reaction initiated by electrochemically generated PINO.<sup>5</sup> But the reaction did not proceed when a free-radical trap (4-butylcatechol) was added to the reaction mixture. In a control experiment (2 h,  $30^\circ\text{C}$  without  $\text{Mn}^{\text{III}}$ TPPCL) the uptake of  $\text{O}_2$  was only  $0.1 \text{ cm}^3$ . The rate of  $\text{O}_2$  consumption was increased when the concentration of  $\text{Mn}^{\text{III}}$ TPPCL was doubled to  $0.28 \text{ mmol dm}^{-3}$ , while reduction in the concentration of styrene from  $120$  to  $60 \text{ mmol dm}^{-3}$  did not affect the rate. In order to determine which of the two compounds, *i.e.*, the carbonyl compound (9) or the hydroxide (8) is more likely to come from the reaction between either the presumed intermediate peroxy radical or the hydroperoxide (I') and  $\text{Mn}^{\text{III}}$ TPPCL, an experiment was performed, in which PINO was generated by the electrolysis of NHPI ( $0.85 \text{ V vs. SCE}$ ) in the presence of styrene and pyridine of the same concentration (as in the typical experiment but without  $\text{Mn}^{\text{III}}$ TPPCL) and the reaction was followed by high performance liquid chromatography (h.p.l.c.). The formation of the hydroxide (8) and the carbonyl compound (9) vs. time are shown in Figure 2 along with the decrease in NHPI. As shown in Figure 2 both compounds (8) and (9) were found to be formed without an induction period. There was no peak in the h.p.l.c. trace which could be assigned to the hydroperoxide (I'). The result shows that the yield of the hydroxide (8) decreased to one third of the typical experimental yield (11%), while that of the carbonyl compound (9) remained almost the same (36%).

Triphenylphosphine was added to the above reaction mixture to examine whether it could be oxidized to triphenylphosphine oxide by the transient peroxy radical (I) or the hydroperoxide (I'). Neither the expected product (triphenylphosphine oxide)

**Table 2.** Oxidation of alkenes catalysed by  $Mn^{III}TPPCL$ .<sup>a</sup>

| Run | [Alkene]/<br>mmol dm <sup>-3</sup> |      | Products yields (%) <sup>b</sup> |                 |          |     |     |     |     |
|-----|------------------------------------|------|----------------------------------|-----------------|----------|-----|-----|-----|-----|
|     | (1)                                | (2)  | (3)                              | (8)             | (9)      | (4) | (5) | (6) | (7) |
| 1   | 25                                 | 120  | 5 <sup>c</sup>                   | <i>d</i>        | <i>d</i> | 8   | 41  | 70  | 20  |
| 2   | 120                                | 0    | 27 <sup>c</sup>                  | 33              | 41       | 11  |     |     |     |
|     | (10)                               | (2)  | (11)                             | (12)            | (13)     |     |     |     |     |
| 3   | 25                                 | 120  | 7                                | <i>d</i>        | <i>d</i> |     | 40  | 197 | 12  |
| 4   | 120                                | 0    | 22                               | 10 <sup>e</sup> | 40       |     |     |     |     |
|     | (14)                               | (2)  | (15)                             | (16)            |          |     |     |     |     |
| 5   | 25                                 | 120  | <i>f</i>                         | <i>d</i>        |          |     | 36  | 58  | 15  |
| 6   | 120                                | 0    | <i>f</i>                         | 34              |          |     |     |     |     |
|     | (1)                                | (17) | (18)                             |                 |          |     |     |     |     |
| 7   | 25                                 | 120  | 40                               |                 |          |     |     |     |     |
|     | (1)                                | (19) | (20)                             | (21)            |          |     |     |     |     |
| 8   | 25                                 | 120  | 25                               | Trace           |          |     |     |     |     |
|     | (1)                                | (22) | (21)                             | (20)            |          |     |     |     |     |
| 9   | 25                                 | 120  | 19                               | 0               |          |     |     |     |     |

<sup>a</sup> The reaction conditions are identical with those mentioned in Table 1.<sup>b</sup> Based on NHPI. <sup>c</sup> Contains small amount of phenylacetaldehyde.<sup>d</sup> Not determined. <sup>e</sup> (12) dissolved in acetonitrile is not stable and releases phthalimide if allowed to stand. <sup>f</sup> Identified but not determined quantitatively due to the instability of epoxide (15).**Table 3.** Effects of pyridine derivatives on the yield of oxide.

| Pyridine derivative  | Yields (%) <sup>a</sup>    |                                 |
|----------------------|----------------------------|---------------------------------|
|                      | Styrene oxide <sup>b</sup> | Cyclo-octene oxide <sup>c</sup> |
| Pyridine             | 27                         | 40                              |
| 2-Methylpyridine     | 20                         |                                 |
| 3-Methylpyridine     | 25                         |                                 |
| 4-Methylpyridine     | 30                         | 45                              |
| 2,6-Dimethylpyridine | 20                         | 22                              |
| 3-Cyanopyridine      | Trace <sup>d</sup>         | 4                               |

<sup>a</sup> Based on NHPI. <sup>b</sup> Under typical reaction conditions. <sup>c</sup> Styrene (25 mmol dm<sup>-3</sup>), cyclo-octene (120 mmol dm<sup>-3</sup>), NHPI (20 mmol dm<sup>-3</sup>),  $Mn^{III}TPPCL$  (0.14 mmol dm<sup>-3</sup>), and a pyridine derivative (80 mmol dm<sup>-3</sup>). <sup>d</sup> Benzaldehyde was formed in 28% yield.

nor an increase in the yield of the hydroxide (8) were observed, which suggests that the life of the peroxide (I) or (I') is very short. In the reactions involving a large excess of styrene, PINO, formed either electrochemically or by  $Mn^{III}TPPCL$ -catalysed autoxidation, would react exclusively with styrene and not with the intermediates or products of the reactions. In fact, the reaction rate of the reaction between PINO and styrene seems to be fast, since the yellow colour of PINO was discharged rapidly on when a solution of it was added to an acetonitrile solution of styrene. Thus the oxidation of the hydroxide (8) to the carbonyl compound (9) by PINO would be almost negligible in both reactions, which is also shown as the parallel increases in the hydroxide (8) and the carbonyl compound (9). These results suggest that in the reaction initiated by  $Mn^{III}TPPCL$  or that initiated by electrochemically generated PINO in the absence of  $Mn^{III}TPPCL$ , almost all of the carbonyl compound (9) is formed essentially through the decomposition of the peroxide (I) or (I') in a way similar to that observed in the oxygenation of alkenes,<sup>4,6</sup> while about two thirds of the

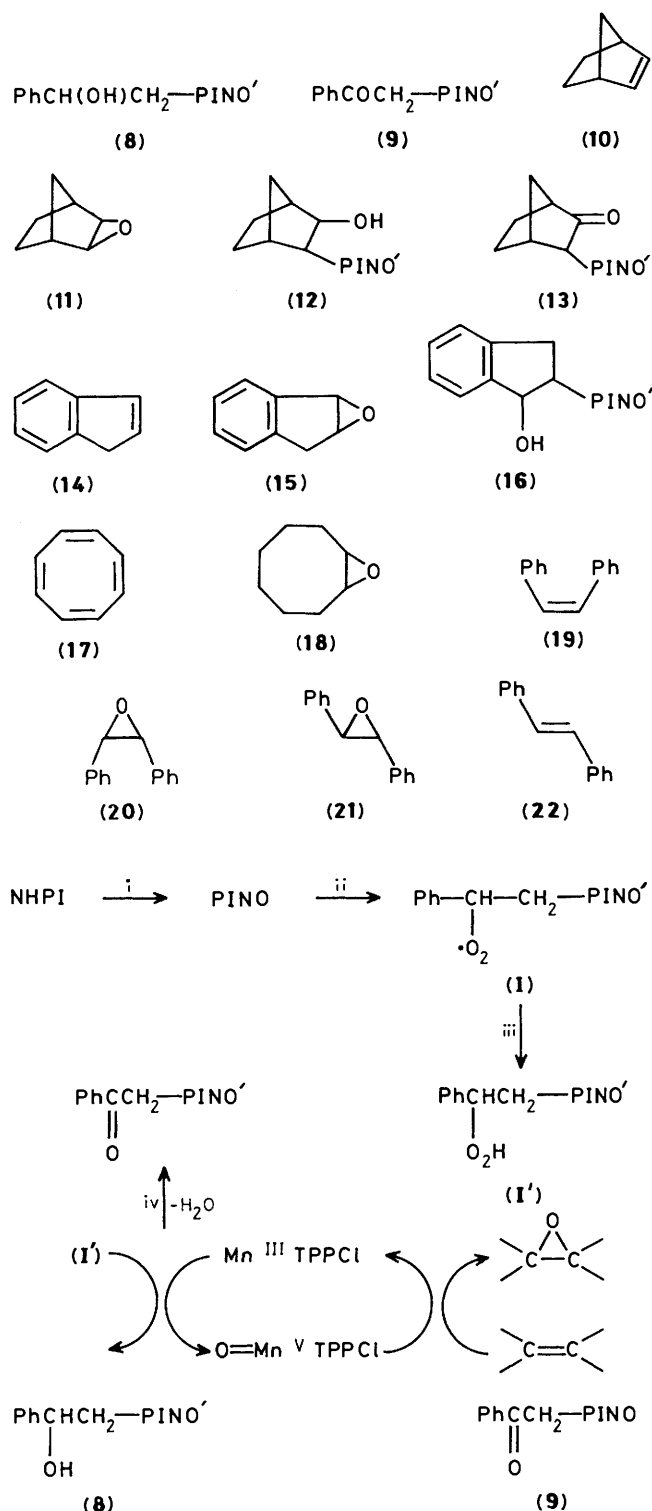
hydroxide (8) formed in the reaction with  $Mn^{III}TPPCL$  results from the reaction between  $Mn^{III}TPPCL$  and the peroxide (I) or (I'). The observation that the yield of the hydroxide (8) increased to 44% and that of the carbonyl compound (9) decreased to 30% in the reaction where a larger amount of cyclohexene oxide was formed (41%, run 2 in Table 1) also supports the theory that hydroxide (8) is produced from the reaction of the peroxide (I) or (I') with  $Mn^{III}TPPCL$  to give  $O=Mn^VTPPCL$ , which would epoxidize cyclohexene. Hence, it seems quite in order to replace the carbonyl compound (II) in Scheme 1 with the corresponding hydroxide (8).

*Epoxidation using Indene or 2-Norbornene Instead of Styrene.*—As mentioned above, the presumed intermediate peroxide (I) or (I') seems to be highly unstable, being converted into the corresponding hydroxide (8) and the carbonyl compound (9) within a very short time. In view of this we performed further experiments to support the intermediacy of the peroxide (I) or (I') by examining the epoxidation using indene or 2-norbornene in place of styrene, since both styrene and indene have been reported to form 2-mercaptoethyl hydroperoxides and 2-mercaptoindan-1-yl hydroperoxides, respectively, in the co-oxidation of styrene or indene with thiols by  $O_2$ , which takes place *via* slow intramolecular rearrangement to 2-sulphinyloxyethanols and 2-sulphinyloxyindan-1-ols, respectively.<sup>7</sup> The homolytic addition of acyl nitroxides is also known to be facile for 2-norbornene.<sup>8</sup> These reports suggest that homolytic addition of PINO to indene or 2-norbornene also occurs in the present system and the resulting adducts undergo attack by  $O_2$  to form the corresponding peroxy radical or hydroperoxide. In addition, these presumed adducts, *N*-(1-hydroperoxyindan-2-yloxy)phthalimide and *N*-(2-hydroperoxybicyclo[2.2.1]heptan-2-yloxy)phthalimide cannot undergo intramolecular monooxygen transfer like that observed in the co-oxidation of styrene or indene with thiols. As a result, when  $Mn^{III}TPPCL$  is present in the reaction, the above hydroperoxides transfer monooxygen to the complex to give  $O=Mn^VTPPCL$ , which then epoxidizes indene, 2-norbornene, or other added alkenes. When epoxidation of indene was examined under the conditions identical with the typical conditions described above, 1,2-epoxyindane and the hydroxide, *N*-(1-hydroxyindan-2-yloxy)phthalimide (34%, run 6 in Table 2) were found to be formed. The carbonyl compound, *N*-(1-oxoindan-2-yloxy) phthalimide was, however, not observed (see the Experimental).

In an experiment using indene as a reagent (run 5), cyclohexene oxide was also formed in a yield comparable to that obtained in the reaction using styrene (run 1). Also, in the case of 2-norbornene, the epoxidation of 2-norbornene itself (run 4) and added cyclohexene (run 3), and the formation of the hydroxide (12) and the carbonyl compound (13) were shown to occur in a manner similar to that observed in the case of styrene. Based on these results, a peroxide of the type (I) or (I') is thought to be present as a common intermediate in every reaction of the present system using styrene 2-norbornene, or indene as the active alkene. The results of epoxidation of other alkenes using styrene as a reagent are also shown in Table 2. The yields of epoxides in cyclic alkenes where the double bond is fixed in the *Z* configuration seem to be better than those of acyclic alkenes.

*Effects of Pyridine Derivatives on the Epoxidation.*—Effects of pyridine derivatives on the yields of styrene oxide and cyclo-octene oxide were examined under the typical conditions using styrene as a reagent (Table 3).

The addition of pyridine derivatives with electron-donating groups on the position experiencing no steric hindrance around the nitrogen atom, increased yields of both oxides. A pyridine derivative with an electron-withdrawing group such as 3-cyano,



Scheme 2. Reagents: i,  $\text{Mn}^{\text{III}}\text{TPPCL}$ -pyridine- $\text{O}_2$ ; ii, styrene- $\text{O}_2$ ; iii,  $\text{NHPI-CH}_3\text{CN}$ ; iv, pyridine.

however, gave quite a different result, namely, that the autoxidation of styrene to benzaldehyde<sup>4</sup> became the main reaction. Styrene oxide was found to be stable enough to resist conversion into benzaldehyde during the reaction in the presence of 3-cyanopyridine. These results seem to be related to the ability of these pyridines to act as manganese ligands. The effect of pyridine derivatives on the yields of oxides and the stereospecific

epoxidation observed in the reaction of (*Z*)- and (*E*)-stilbene (Table 2) support the theory that an oxomanganese intermediate similar to that involved in the metalloporphyrin-catalysed epoxidation<sup>9</sup> is involved in the present system.

### Conclusion

Based on the results mentioned above, we propose a partly revised reaction route for the epoxidation discussed using styrene as an active alkene, in which the carbonyl compound (II) in the former scheme (Scheme 1) is replaced by the hydroxide (8), though the direct observation of the high-valent oxomanganese complex (see the Experimental) and the hydroperoxide (I') has not yet been successful.

The observation that there was no consumption of  $\text{O}_2$  and  $\text{NHPI}$  in the absence of any of the other three agents ( $\text{NHPI-Mn}^{\text{III}}\text{TPPCL}$  or pyridine- $\text{O}_2$ ,  $\text{Mn}^{\text{III}}\text{TPPCL}$  or pyridine, respectively) shows that both pyridine and  $\text{Mn}^{\text{III}}\text{TPPCL}$  work not only in the catalytic epoxidation cycle but also to help the autoxidation of  $\text{NHPI}$  to  $\text{PINO}$ . The rate for oxidation of  $\text{NHPI}$  seems to be slower than the reaction of  $\text{PINO}$  to (I), since increased concentration of  $\text{Mn}^{\text{III}}\text{TPPCL}$  increased the rate of consumption of  $\text{O}_2$ , while increased concentration styrene, which is present in large excess, did not effect the rate. Other alkenes such as oct-1-ene and 2-methylhept-1-ene were examined to see whether they are as effective as the above alkenes for the epoxidation using cyclohexane as a substrate. They gave the results which are very similar to that observed in the reaction without styrene (runs 3 and 4, Table 1), showing that  $\text{Mn}^{\text{III}}\text{TPPCL}$ -catalysed autoxidation of cyclohexane was the only reaction observed. In the case of oct-1-ene, considerable amount of oct-1-en-3-one was detected, which was probably formed through  $\text{PINO}$ -induced autoxidation.<sup>5b</sup> The present investigation suggests that transient peroxides, which are formed by the co-oxidation of alkenes such as styrene, 2-norbornene or indene with  $\text{NHPI}$ , are able to operate as mono-oxygen donors to  $\text{Mn}^{\text{III}}\text{TPPCL}$  in a way similar to compounds bearing activated oxygen e.g., hydroperoxides, peracids, iodosoarenes, or sodium hypochlorite, which have been used in model systems of cytochrome P-450 enzymes.

### Experimental

**Instrumentation.**—Gas-chromatographic analyses (g.l.c.) were performed on a JEOL JGC-20K fitted with a PEG 20M glass column (2 m; 3 mm diameter) and equipped with FID. High performance liquid chromatographic (h.p.l.c.) analyses were performed on a Shimadzu LC-5A fitted with Water Associates Radical-PAK ( $\mu$  BONDAPAK  $\text{C}_{18}$ ) equipped with spectrophotometric detector SPD-2A.  $^1\text{H}$  N.m.r. spectra were recorded on a Hitachi R-60 spectrometer in the Fourier transform mode with  $\text{Me}_4\text{Si}$  as an internal standard. I.r. spectra were recorded on a JASCO A-202 spectrophotometer. Visible and ultraviolet absorption spectra were recorded on a Hitachi 124 spectrophotometer. Controlled potential electrolysis was carried out with a Hokuto Denko HA 101 potentiostat equipped with a Hokuto Denko HF 102 coulometer.

**Materials.**—Cyclohexene, cyclo-octene, 2-norbornene, (*E*)-stilbene (Nakarai Chemicals), styrene (Wako Chemicals), indene (Tokyo Kasei Kogyo) and (*Z*)-stilbene (Aldrich Chemical Co.) were purchased and ascertained by g.l.c. to be free from their epoxides prior to use. Styrene oxide, cyclohexene oxide, cyclohex-2-en-1-ol, phenylacetaldehyde and *N*-hydroxyphthalimide (Tokyo Kasei Kogyo), (*E*)- and (*Z*)-stilbene oxide and  $\text{Mn}^{\text{III}}\text{TPPCL}$  (Aldrich Chemical Co.) were purchased and used as received. Cyclo-octene oxide,<sup>10,11</sup> 2,3-epoxybicyclo[2.2.1]heptane,<sup>11</sup> and 2,3-epoxy-2,3-dihydroindene<sup>12</sup> were

prepared according to the known methods described in the literature.

Commercially available 2- and 3-methylpyridine, 3-cyanopyridine (Nakarai Chemicals), 4-methylpyridine, 2,6-dimethylpyridine (Wako Chemicals) were used as received.

**Epoxidation: Typical Experiment and Product Analysis.**—Epoxidation of styrene, 2-norbornene, or indene in a typical experiment was performed in acetonitrile (20 cm<sup>3</sup>) containing each alkene (120 mmol), NHPI (20 mmol), pyridine (20 mmol), and Mn<sup>III</sup>TPPCL (0.14 mmol) under an atmosphere of air at 30 °C with mechanical stirring. All reactions under these conditions complete within *ca.* 3 h. In the reactions where styrene, 2-norbornene or indene were used as the agent, each of the three alkenes (25 mmol) were added to an acetonitrile solution of the substrate (120 mmol dm<sup>-3</sup>) and the other usual reagents. All epoxides, cyclohex-2-enone, and cyclohex-2-enol were determined by g.l.c. The *cis:trans* ratio in the epoxidation of (*Z*)- and (*E*)-stilbene was determined by <sup>1</sup>H n.m.r. spectroscopy using crude products after passage of the reaction mixture through a silica-gel column. The carbonyl compounds (**9**) and (**13**) and the hydroxides (**8**), (**12**), and (**16**) were determined by h.p.l.c. using the compounds separated from the larger-scale reactions (see below) as authentic samples.

**Oxidation of Styrene on a Large Scale.**—Mn<sup>III</sup>TPPCL (18 mg, 0.025 mmol) was added to a stirred acetonitrile solution (100 cm<sup>3</sup>) containing styrene (1.44 g, 13.8 mmol), NHPI (2.0 g, 12.3 mmol) and pyridine (1 g, 12.6 mmol). After being stirred for 20 h at room temperature, the acetonitrile and pyridine were evaporated off under reduced pressure. The residual sticky oil contained at least six products (t.l.c.) including Mn<sup>III</sup>TPPCL and NHPI remained unchanged, which were separated by column chromatography (silica gel). These were eluted out in the order: styrene oxide, the hydroxide, *N*-(2-hydroxy-2-phenylethoxy)phthalimide (**8**), the carbonyl compound, *N*-benzoylmethoxyphthalimide (**9**) and NHPI, with hexane–AcOEt (7:1).

(**8**): Viscous oil, showing ABX type <sup>1</sup>H n.m.r. spectrum, δ(CDCl<sub>3</sub>) 4.05 (1 H, s, OH, disappeared on addition of D<sub>2</sub>O), 4.06 (1 H, dd, H<sub>A</sub>), 4.40 (1 H, dd, H<sub>B</sub>), 5.02 (1 H, dd, H<sub>X</sub>), 7.30 (5 H, s, Ph), and 7.76 (4 H, s, Ph) (Found: C, 67.45; H, 4.6; N, 5.05%. C<sub>16</sub>H<sub>13</sub>O<sub>4</sub>N requires C, 67.8; H, 4.62; N, 4.94%).

(**9**) M.p. 128 °C (lit.,<sup>13</sup> 135 °C), δ(CDCl<sub>3</sub>) 5.41 (2 H, s, CH<sub>2</sub>) and 7.25–8.15 (9 H, m, Ph).<sup>13</sup>

**Oxidation of 2-Norbornene or Indene on a Large Scale.**—Oxidation and products separation were performed following almost the same procedure as that for the oxidation of styrene. In the case of 2-norbornene, the carbonyl compound, *N*-(2-oxobicyclo[2.2.1]heptan-3-yloxy)phthalimide (**13**) was eluted before the hydroxide, *N*-(2-hydroxybicyclo[2.2.1]heptan-2-yloxy)phthalimide (**12**).

(**12**): Needle crystals from AcOEt, m.p. 118–120 °C, δ(CDCl<sub>3</sub>) 1.0–2.30 (8 H, m, 1-, 4-, 5-, 6-, 7-H), 2.65 (1 H br, 2-H), 3.95 (2 H, m, 3-H and OH), and 7.80 (4 H, s, Ph) (Found: C, 65.7; H, 5.26; N, 5.42%. C<sub>15</sub>H<sub>15</sub>N<sub>1</sub>O<sub>4</sub> requires C, 65.9; H, 5.53; N, 5.12%).

(**13**): Amorphous solid from AcOEt–hexane, m.p. 133–136 °C, δ(CDCl<sub>3</sub>) 0.89–2.70 (8 H, m, 1-, 4-, 5-, 6-, 7-H), 4.15 (1 H, d, 2-H), and 7.76 (4 H, s, Ph). This compound is not very stable and decomposes to phthalimide (elemental analysis) when it is dried under vacuum at 50 °C (Found: C, 65.5; H, 4.53; N, 5.29%. C<sub>15</sub>H<sub>13</sub>N<sub>1</sub>O<sub>4</sub> requires C, 66.4; H, 4.83; N, 5.16%).

*N*-(3-Hydroxyindan-2-yloxy)phthalimide (**16**) as amorphous solid from AcOEt m.p. 122–124 °C; δ(CDCl<sub>3</sub>) 3.10 (1 H, br, OH), 3.30 (2 H, dd, CH<sub>2</sub>), 4.85 (1 H, dd, CHON), 5.51 (1 H, d, CHOH), 7.05 (4 H, m, Ph), and 7.60 (4 H, s, Ph) (Found: C, 69.0; H, 4.22; N, 4.83%. C<sub>17</sub>H<sub>13</sub>N<sub>1</sub>O<sub>4</sub> requires C, 69.1; H, 4.40; N,

4.74%). The formation of another expected compound, *N*-(3-oxoindan-2-yloxy)phthalimide was not ascertained, since it could not be isolated from the large-scale oxidation reaction mixture by column chromatography.

**Procedure for Measuring O<sub>2</sub> Uptake.**—Acetonitrile (30 cm<sup>3</sup>) containing all of the reagents in the same concentration as described in the typical procedure, with the exception of pyridine was placed in a vessel attached to a gas burette and O<sub>2</sub> supply, and flushed with O<sub>2</sub> for 5 min. The uptake was followed after the addition of pyridine dissolved in acetonitrile by means of a needle inserted through a serum stopper.

**Attempted Observation of the Transient Species.**—(a) The observation of a high-valent Mn–oxo species characterized by a Soret peak at 426 nm<sup>14</sup> in the visible light spectrum was attempted by adding styrene (2 mmol dm<sup>-3</sup>) to the same concentration of NHPI in acetonitrile in a 1 mm cuvette containing Mn<sup>III</sup>TPPCL (0.14 mmol) and pyridine (80 mmol). The reaction led to a small reduction of the peak height at 475 nm characterized as Mn<sup>III</sup>TPPCL,<sup>14</sup> but did not lead the appearance of peak at 426 nm.

(b) Acetonitrile solution containing PINO which was prepared by electrochemical oxidation of NHPI (4 mmol dm<sup>-3</sup>) was added to acetonitrile solution containing styrene (4 mmol dm<sup>-3</sup>) and Mn<sup>III</sup>TPPCL (0.07 mmol dm<sup>-3</sup>) placed into a spectrometer. The result was nearly the same as that observed in (a).

**Reaction of Styrene and PINO generated by Electrochemical Oxidation of NHPI.**—NHPI in acetonitrile (20 mmol dm<sup>-3</sup>; 20 cm<sup>3</sup>) containing pyridine (80 mmol dm<sup>-3</sup>), styrene (120 mmol dm<sup>-3</sup>) and NaClO<sub>4</sub> (0.1 mmol dm<sup>-3</sup>) as a supporting electrolyte was electrolysed at 0.85 v *vs.* SCE using glassy-carbon plates as the electrodes under an atmosphere of air, in an undivided cell, with mechanical stirring. The reaction was followed by h.p.l.c. of samples taken from several stages of the electrolysis.

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