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Chemoselective epoxidation of dienes using polymer-supported manganese porphyrin catalysts

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Abstract—Manganese porphyrin catalysts supported on different polymer resins were assessed in the selective epoxidation of three dienes. The recyclability of the catalysts was examined. © 2004 Elsevier Ltd. All rights reserved.

1. Introduction

Heterogeneously-supported manganese porphyrins have been widely investigated as catalysts in the epoxidation of alkenes. A survey of the literature revealed that these catalysts are most efficient in the epoxidation of conjugated alkene substrates (most commonly styrene and indene), followed by cyclic alkenes (cyclohexene, cyclooctene). In contrast, they are less successful in catalysing the epoxidation of less electron-rich terminal olefins such as dodec-1ene and 1-hexene. Hence, in principle, supported manganese porphyrins may show good chemoselectivity in epoxidation of substrates containing more than one type of alkene. Although limonene has been widely chosen as a substrate to probe the steric hindrance of synthetic metalloporphyrins,¹⁻³ other dienes and polyolefins are rarely examined as substrates.

Previously, we immobilised the manganese complex of 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin**1**on Merrifield and Argogel resins and examined their subsequent catalytic activity in the epoxidation of a wide range of mono-alkenes (styrene, stilbene, methylstyrene, cyclo-octene, cyclohexene, norbornene, hex-1-ene and dodec-1-ene).⁴ During the study, we discovered important compatibility issues between the nature of the linker group and catalyst activity and stability. The Merrifield resin-supported catalyst has been demonstrated to be robust, and may be subjected to several successive catalytic reactions without leaching. However, rates of turnover were slow,

which we attributed to restricted mobility of the reactive metalloporphyrin moiety, imposed by the short spacer between the support and the catalyst. On the other hand, the flexible PEG spacer afforded by the Argogel-supported catalyst was found to be unstable, and extensive leaching was observed during catalytic recycling.

In this paper, we report the preparation of two new catalysts from commercially available polymer supports with more robust and longer linkers. These were compared with the Merrifield-supported catalyst in the chemoselective epoxidation of three types of dienes. Recyclability and selectivity of these catalysts were compared and contrasted.

2. Results and discussion

2.1. Catalyst preparation

Following previously reported procedures,⁴ porphyrin **1** was tethered to commercially available Merrifield, bromo-Wang and carboxy bromo-Wang resins via an ether linkage, by treating the chlorinated/brominated resin beads with 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin **1**, in the presence of K_2CO_3 at 80 °C for three days (Scheme 1)— Irori KanTM reactors were used to protect the polymer beads from structural damage that may arise through prolonged mechanical stirring. Functionalized polymer supports **2–4** were thus obtained as dark purple beads. The reactions were monitored by following the displacement of the halide (%Cl or %Br analysis), whereas the final yields of the reactions were calculated from %N content. With the exception of **3**, yields were typically high. Subsequent metallation of the supported porphyrins **2–4** with MnCl₂ at high temperature

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Scheme 1. Preparation of manganese porphyrins supported on commercially available resins: (a) Merrifield (2)/bromo-Wang (3)/carboxy bromo-Wang (4), K_2CO_3 , DMF, 80 °C, 3 days; (b) MnCl₂ (50 equiv.), DMF, 165 °C, 2.5 h.

afforded the four supported manganese porphyrins **5**, **6** and **7**, respectively. Complexation was indicated by the disappearance of the ν (N–H) absorption band in the single-bead transmittance FTIR spectrum. The catalytic loading of the polymer beads, verified by %Mn analysis (ICP-AES), was between 0.26 and 0.53 mmol/g.

2.2. Catalytic epoxidation of dienes and recycling studies

Three diene substrates were chosen in the catalytic study (Fig. 1): 1,5-cyclooctadiene, 7-methyl-1,6-octadiene and limonene. Using previously optimised conditions (Scheme 2), the epoxidation reactions were performed employing 4 mol% of catalyst in the presence of imidazole, with sodium periodate as the oxidant.



Figure 1. Chosen substrates for the chemoselective epoxidation.



Scheme 2. General reaction conditions employed for catalytic epoxidation.

2.3. Epoxidation of 7-methyl-1,6-octadiene (Table 1, entries 1–3)

From previous studies, we expect the more electron-rich double bond to be epoxidised more favourably over the terminal alkene. Indeed, this proved to be the case (Table 1, entries 1-3). Tri-substituted epoxide was obtained exclusively in high yields (91–100%) in all cases.

 Table 1.
 Selective epoxidation of 7-methyl-1,6-octadiene and cyclooctadiene

Entry	Substrate	Product	Catalyst	T/h	Yield/% ^a
1	$\gamma \gamma \gamma \gamma_{3} \gamma$	γ	5	33	94
2 3		, , , , , , , , , , , , , , , , , , ,	6 7	33 24	91 100
4		0	5	36	76
5 6 7 8			6 7	42 36 36 36	68 ^b 63 76 ^c 51 ^{b,d}

Reaction conditions outlined in Scheme 2.

^a GC yields with respect to starting material.

^b Carried out with recovered catalyst.

^c Bis-epoxide (9%) was observed after 6 h.

^d Formation of bis-epoxide was not observed in the second cycle.

Monitoring the progress of the reactions by GC (Fig. 2), the presence of an induction period of 4 h was detected before the Merrifield-supported catalyst **5** commenced its turnover. Beyond this, its activity was roughly comparable to that of Wang-supported **6**, which appeared to be the least robust, as its turnover ceased after 30 h. In contrast, the carboxy-Wang supported catalyst **7** gave the highest and quickest turnover, achieving 97% conversion within 12 h.



Figure 2. Rate of conversion of 7-methyl-1,6-octadiene catalysed by $5(\blacklozenge)$, $6(\blacksquare)$ and $7(\blacklozenge)$.

2.4. Epoxidation of cyclooctadiene (Table 1, entries 4-8)

1,5-Cyclooctadiene contains two identical double bonds, from which it is possible to obtain mono- and bis-epoxide products. Most oxidants tend to reduce the diene to a mixture of products, including diols and ketones. Whilst the peroxide-based oxidants (such as that catalysed by MTO) tend to yield the bis-epoxide,^{5,6} the synthetically more useful mono-epoxide may be obtained by the epoxidation of the diene by peracids, with yields of between 40 and 72%.^{7,8}

A prior study by Jørgensen deployed an iron(II) phthalocyanine/iodosylbenzene system in the epoxidation of 1,5-cyclooctadiene, which led to the formation of a mixture of oxidised products in low yields.⁹ In light of this, it was somewhat surprising to find that highly selective monoepoxidation may be achieved using supported manganese porphyrins. Catalysts **5** and **6** gave exclusive formation of the mono-epoxide (Table 1, entries 4–6), whereas a small formation of bis-epoxide was observed with catalyst **7** (entry 7). In the latter case, the presence of the bis-epoxide was detected after 6 h.

Since catalysts **5** and **7** exhibited similar turnovers (entries 4 and 7), these were recovered by filtration. UV analysis of the reaction mixture (filtrate) did not exhibit any discernable absorption peaks that may be attributed to free or manganese porphyrin, thus indicating that no leaching of the catalyst occurred; the %Mn content of the recovered beads was also similar to the original value. The recovered catalysts were thus subjected to a second catalytic run. Both of the recycled catalysts showed much reduced catalytic activity (Table 1, entries 4 vs. 5, 7 vs. 8). In the reaction catalysed by recovered carboxy-Wang supported catalyst **7**, the slower turnover evidently suppressed the formation of the bis-epoxide.

2.5. Epoxidation of limonene

The monoterpene limonene contains an internal trisubstituted double bond and a disubstituted terminal double bond, and has been widely studied as a substrate in porphyrin epoxidation chemistry. Bis-epoxide may be obtained from simultaneous epoxidations, and the formation of 1, 2- and/or 8, 9-limonene oxides 8 and 9 (Scheme 3) was commonly used to denote the selectivity of the process, generally taken to reflect the steric environment of the metalloporphyrin.²



Scheme 3. Epoxidation of limonene.

Immobilisation of manganese porphyrin catalysts typically leads to a catastrophic effect on their selectivity towards the epoxidation of limonene, lowering the ratio from 9:1 in favour of the 1,2-epoxide **8**, to typically less than $1.7:1.^{10}$ The most selective supported manganese catalyst reported to date is a Mn(III) porphyrin ionically bound to poly(4-styrylmethyl)pyridinium chloride, which gave an overall yield of 91% in a 3:1 ratio.

Generally speaking, the covalently-bound manganese porphyrins 5-7 gave fairly comparable results, with ratios greater than 2:1 in most cases (Table 2). The selectivity of the process appeared to be dependent on the amount of oxidant employed. For catalysts 5 and 6, a 2:1 oxidant-to-alkene ratio seemed to be optimal for both activity and selectivity (entries 1-3 and 4-6). In contrast, carboxy-Wang supported manganese porphyrin 7 appeared to be more robust, since the amount of oxidant did not affect its activity significantly. The highest chemoselectivity of 2.7:1 was obtained with catalysts 6 and 7 (Entries 5 and 7) with yields of between 66 and 68%. A small amount of the bisepoxide was formed during the catalytic reaction employing catalyst 7.

Table 2. Epoxidation of (R)-limonene

Entry	Catalyst	Oxidant:diene ratio	Time (h)	Yields 8:9 ^a	Ratio 8:9
	_		24	12.0	
1	5	3:1	24	12:9	1.3:1
2	5	2:1	24	52:23	2.3:1
3	5	1:1	24	38:20	1.9:1
4	6	3:1	24	43:24	1.8:1
5	6	2:1	24	48:18	2.7:1
6	6	1:1	24	42:24	1.8:1
7	7	3:1	24	50:18	2.7:1
8	7	2:1	24	51:22 ^b	2.3:1
9	7	1:1	24	30:16	1.9:1

Reaction conditions as outlined in Scheme 2, except for the amount of oxidant.

^a GC yield with respect to starting material. No diastereomeric excess was observed in either product.

^b 6% Bis-epoxide.

Once again, catalyst 7 was found to be the most active, compared to the other two catalysts. Under these conditions, the maximum yield of the 1,2-epoxide was reached within 12 h, whereupon the formation of the bis-epoxide became apparent, which coincides with the drop in yield (Fig. 3).



Figure 3. Rate of formation of 1,2-limonene epoxide 8 with catalyst 7.

The diastereomeric ratio of products 8 and 9 was found to be 1:1 in each case, i.e. the inherent chirality of the starting material did not induce any facial selectivity in the epoxidation of either of the prochiral alkene moieties.

Finally, recyclability of the immobilised catalysts was tested by subjecting **5** and **7** to four successive catalytic

Table 3. Recycling catalysts 5 and 7 for the epoxidation of limonene

Entry	Catalyst (mol%)	Run	Time (h)	Yields 8:9 ^a	Ratio 8:9
1	E (4)	1	24	50.02	2.2.1
1	5 (4) 5 (4)	1	24	52:25	2.3:1
2	5 (4)	2	30	40:20	2.0:1
3	5 (8)	2	24	54:19	2.8:1
4	5 (8)	3	36	60:26	2.3:1
5	5 (8)	4	36	48:17	2.8:1
6	7 (4)	1	24	51:22 (6 ^b)	2.3:1
7	7 (4)	2	24	48:23	2.1:1
8	7 (8)	2	36	50:20	2.0:1
9	7 (8)	3	36	57:26	2.2:1
10	7 (8)	4	36	53:22	2.4:1

Oxidant/limonene (2:1).

^a GC yields with respect to limonene. No diastereomeric excess was observed in either product.

^b Bis-epoxide.

reactions (Table 3). For the Merrifield-supported porphyrin 5, the recovered catalyst became increasingly less active requiring either longer reaction times (entries 1 vs. 2 and 2 vs. 3) or higher catalytic loading (entries 2 vs. 3) to achieve comparable yields. In sharp contrast, catalyst 7 may be reused with no significant loss in activity in all four cycles (entries 8–10). Also, competitive formation of the bisepoxide was not observed after the first catalytic run.

Remarkably, the selectivity was broadly maintained between the different cycles, and both catalysts may be subjected to four consecutive runs without significant changes in the $\geq 2:1$ ratio.

3. Conclusion

To conclude, we have prepared and examined the comparative catalytic activity, selectivity and reusability of three polymer-supported manganese porphyrins 5-7. Good chemoselectivity was observed in the epoxidation of three cyclic and acyclic dienes. Catalyst 7 consistently excelled in its catalytic activity and selectivity. As the length of the linkers was identical between catalysts 6 and 7, we attribute its superiority to the higher reactive surface area of its beads (200–400 mesh), compared to the other two catalysts (100–200 mesh). All three resins may be recycled with varying successes, but encouragingly, no decline in selectivity was observed.

This work has led us to develop a new class of supported manganese porphyrin catalysts with improved selectivity and catalyst activity, which will be reported in due course.

4. Experimental

4.1. Materials

All resins were purchased from Novabiochem Wang bromo polystyrene and Merrifield resins are 1% cross-linked with bead sizes between 100 and 200 mesh. Brominated Wang resin was 1% cross-linked with bead sizes between 200 and 400 mesh. Anhydrous DMF was purchased from Aldrich and dichloromethane was freshly distilled from CaH₂ under nitrogen. Commercially available chemicals were purchased from Aldrich, Avocado, BDH, Fluka or Lancaster, and were used as received, unless otherwise stated. Manganese dichloride was purchased from Aldrich (99.999% purity).

The MacroKanTM used in the immobilisation of porphyrins is made of polypropylene with an internal volume of 2.4 mL, purchased from Irori Europe Limited (Tarporley Business Centre, Cheshire CW6 9UT, UK).

4.2. Instrumentation

Infrared spectra were recorded on a Perkin Elmer Spectrum One spectrometer. Spectra of porphyrin and metalloporphyrin samples were recorded as solutions in CCl_4 and $CHCl_3$, respectively, within a sealed cell with a path length of 0.1 mm with NaCl windows. Single bead FT-IR spectra (transmittance) were recorded with a beam-condensing accessory (BCA), using a diamond compressor to flatten the bead. UV spectra were recorded on a Perkin Elmer Lambda 18 spectrometer and performed in a thermostated (25 °C) cell of 10 mm path length. The samples were analysed in dichloromethane or in a solution of 20% piperidine in DMF.

¹H and ¹³C NMR spectra were recorded using Bruker AM 360 and AVANCE 400 spectrometers NMR spectra of polymers were recorded using a Bruker AVANCE 400 spectrometer fitted with a special HR-MAS probe, with the resin placed in a 4 mm rotor. Chemical shifts were recorded in parts per million (δ : ppm) referenced to TMS (δ : 0) as an internal standard.

Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded using the EPSRC MS Services at University of Swansea, Wales or the Mass Spectrometry Service within the Department of Chemistry, King's College. FAB MS was run on a KRATOS 'MS89OMS' spectrometer. ES MS was run on a Micromass 'Q-TOF'. GC-MS spectra were recorded on a Varian Saturn 220 spectrometer equipped with an autosampler using a CP-Sil 8CB column.

4.3. Services

Elemental analyses were carried out by the Elemental Analysis Services at the University of North London (C, H, N) or University College London (halogens). %Mn was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) by Medac Ltd.

4.3.1. Synthesis of 4-(10,15,20-triphenyl-porphyrin-5-yl)phenol 1.¹¹ To a refluxing solution of propionic acid (500 mL), were added pyrrole (13.9 mL, 0.2 mol), benzaldehyde (15.3 mL, 0.15 mol) and *p*-hydroxybenzaldehyde (6.1 g, 0.05 mol). The reaction mixture was stirred at reflux for 40 min. Propionic acid was then removed under vacuum. The black residue was first purified by column chromatography on silica, eluting with chloroform. The fraction containing TPPOH was suspended in CH₃OH, filtered and washed with CH₃OH to give 1.6 g (2.53 mmol, 5%) of the desired porphyrin as a purple solid, which was used in the subsequent steps without further purification. $R_{\rm f}$ 0.36 (CHCl₃); mp (220 °C. ¹H NMR (360 MHz, CDCl₃, 20 °C): δ 8.91–8.86 (m, 8H, H₇ and H₈-porphyrin), 8.23 (d, 6H, ³*J*=7.6 Hz; H₂-Ph), 8.10 (d, 2H, ³*J*=8.3 Hz; H₂-Ar), 7.80– 7.75 (m, 9H; H₃-Ph, H₄-Ph), 7.22 (d, 2H, ³*J*=8.3 Hz; H₃-Ar), 5.01 (s, 1H; OH), -2.76 (s, 2H; NH). ¹³C NMR (90.5 MHz, CDCl₃, 20 °C): δ 155.8, 142.6, 136.1, 135.0, 132.0–131.0, 128.1, 127.1, 120.5, 114.1. UV–Vis (CH₂Cl₂): $\lambda_{\text{max/nm}}$ (ε): 415 (103 557), 515 (8461), 550 (3680), 589 (2152), 647 (2077) nm. HR-MS (FAB) (*m*/*z*): calcd for 630.2420, found: 630.2412 [M⁺]. IR (CCl₄, cm⁻¹) ν_{NH} 3313, ν_{OH} 2962.

4.4. General procedure for the synthesis of Merrifield and Wang supported 4-(10,15,20-triphenyl-porphyrin-5yl)-phenols

A Macro Irori KanTM containing the appropriate resin (0.45 mmol) was placed in a N₂ purged three-necked round bottom flask with K₂CO₃ (0.34 g, 2.47 mmol), KI (0.164 g, 0.99 mmol) and *p*-4-(10,15,20-triphenyl-porphyrin-5-yl)-phenol **1** (0.47 g, 0.742 mmol). Anhydrous DMF (20 mL) was added via syringe and the mixture was magnetically stirred at 80 °C for 3 days. After cooling to room temperature, the beads were transferred to a sintered tube and washed successively with acetone/CH₃OH (1:1) (5 mL×5), acetone/CH₃OH/H₂O (1:1:1) (5 mL×5), acetone/CH₃OH (1:1) (5 mL×5), ethyl acetate (5 mL×5), CH₂Cl₂ (3 mL×5) and HPLC-grade pentane (5 mL×5). The resin was dried under vacuum at 50 °C for 2 h to give dark purple beads.

4.4.1. Merrifield 4-(10,15,20-triphenyl-porphyrin-5-yl)phenol 2. Yield=93%, based on %N. After two treatments, elemental analysis found for a loading of 0.52 mmol g^{-1} Cl 0, N 2.90%; HR-MAS ¹H NMR (400 MHz, CDCl₃, 20 °C): δ 8.80 (br s, 8H, H₇ and H₈-porphyrin), 8.14 (br s, 6H, H₂-Ph), 7.59 (br s, 9H, H₃-Ph, H₄-Ph), 7.30–6.50 (br s, PS, H₃-Ar, H₂-Ar), 4.95 (br s, 2H, OCH₂), 1.8 (br s, PS), 1.39 (br s, PS), -2.75 (br s, 2H, NH); FT-IR (cm⁻¹): ν_{NH} 3317.

4.4.2. Wang 4-(10,15,20-triphenyl-porphyrin-5-yl)phenol 3. Yield=37%, based on %N. After two treatments, elemental analysis found for a loading of 0.32 mmol g⁻¹ Br 6, N 1.76%; FT-IR (cm⁻¹): $\nu_{\rm NH}$ 3317 cm⁻¹.

4.4.3. Carboxy-Wang 4-(10,15,20-triphenyl-porphyrin-5-yl)-phenol 4. Yield=85%, based on %N. After one treatment, elemental analysis found for a loading of 0.53 mmol g⁻¹ Br 0, N 2.93%. HR-MAS ¹H NMR (400 MHz, CDCl₃, 20 °C): δ 8.85 (br s, 8H, H₇ and H₈-porphyrin), 8.21 (br s, 6H, H₂-Ph), 7.71 (br s, 9H, H₃-Ph, H₄-Ph), 7.08-6.62 (br s, PS, H₃-Ar, H₂-Ar), 5.36 (br s, 2H, OCH₂), 1.59-1.33 (br s, PS), -2.78 (br s, 2H, NH); FT-IR (cm⁻¹): ν_{NH} 3319, ν_{CO} 1695.

4.5. General procedure for the synthesis of the supported manganese 4-(10,15,20-triphenyl-porphyrin-5-yl)-phenols

In an oven-dried three-neck flask equipped with an overhead stirrer and purged with N₂, the appropriate supported *p*-4-(10,15,20-triphenyl-porphyrin-5-yl)-phenol (0.5 mmol) was stirred in anhydrous DMF (30 mL). The flask was heated to 158 °C for 5 min before manganese chloride (3.13 g, 25 mmol) was added in one portion. The mixture was then stirred at 60 rpm at reflux for 2.5 h. After cooling to room

temperature, the beads were transferred to a sintered tube and washed with CH_2Cl_2 (5 mL×10) and HPLC-grade pentane (5 mL×10). The resin was dried under vacuum at 50 °C for 2 h to give dark purple beads.

4.5.1. Merrifield 4-(10,15,20-triphenyl-porphyrin-5-yl)phenol manganese chloride 5. 100% metallation, based on Mn%; elemental analysis found for a loading of 0.52 mmol g^{-1} , Mn 2.86%.

4.5.2. Wang 4-(10,15,20-triphenyl-porphyrin-5-yl)phenol manganese chloride 6. 100% metallation, based on Mn%; elemental analysis found for a loading of 0.32 mmol g^{-1} , Mn 1.76%.

4.5.3. Carboxy Wang 4-(10,15,20-triphenyl-porphyrin-5-yl)-phenol manganese chloride 7. 100% metallation, based on Mn%; elemental analysis found for a loading of 0.53 mmol g^{-1} , Mn 2.92%. FT-IR (cm⁻¹): ν_{CO} 1695.

4.6. General epoxidation procedure

In a round-bottomed flask or in a Radley's carousel reaction tube, the appropriate catalyst (0.01 mmol), alkene (0.23 mmol) and axial ligand (0.1 mmol) were stirred in CH₃CN (3.7 mL) at room temperature. In a separate flask, NaIO₄ (0.46 mmol) was dissolved in H₂O (1.85 mL). This aqueous solution of NaIO₄ was transferred to the catalytic mixture. The progress of the reaction was monitored at regular intervals by analysing extracted aliquots by GC-MS. The yields of epoxides were based on the starting material consumed.

5. General procedure for the recovery and reuse of the catalyst

At the end of the epoxidation, the polymer-supported catalyst was filtered off via a filter syringe. The filtrate was extracted with CH_2Cl_2 , washed with water, dried over Na_2SO_4 and evaporated. A small amount of the residue obtained was dissolved in dichloromethane and analysed by UV spectroscopy to determine if leaching of the porphyrin from the support had occurred. The catalyst beads in the syringe were washed with water, CH_2Cl_2 and HPLC-grade pentane and then dried under vacuum at 50 °C for 2 h. The recovered catalyst was then subjected to another catalytic cycle as described above.

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