Pergamon

Tetrahedron Letters 43 (2002) 8555–8558

TETRAHEDRON
LETTERS

Supported manganese porphyrin catalysts as P450 enzyme mimics for alkene epoxidation

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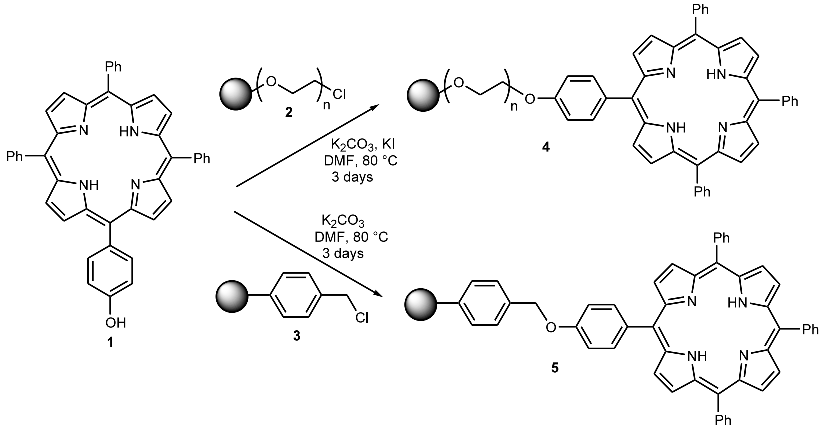
Received 26 June 2002; revised 9 September 2002; accepted 19 September 2002

Abstract—Manganese porphyrin catalysts have been supported on Merrifield and Argogel resins and their catalytic activity has been demonstrated in alkene epoxidation. Furthermore, recyclability studies have shown that the reuse of the Merrifield-supported catalyst can be achieved three times with minimum loss of activity. © 2002 Published by Elsevier Science Ltd.

Major advances in the development of supported catalysts for organic reactions have been achieved and this has been reflected in a number of in-depth reviews.[1] In particular, there has been great activity in the field of supported catalysts for alkene epoxidation.[1a,2] P450 enzyme mimics[3] based on metalloporphyrins have been studied as epoxidation catalysts, however they readily undergo decomposition (due to self-oxidation) in solution phase. Therefore, attachment of these catalysts to insoluble supports is particularly attractive as it should prevent this deactivation process. Further advantages of immobilisation include simplified procedures for product purification and catalyst recovery. Moreover, recent interest in supported metalloporphyrin catalysts[4–13] for olefin epoxidation prompts us to report our studies in this area.

Here we report the synthesis of a new Argogel-supported manganese porphyrin **7**, as well as its catalytic activity in the epoxidation of a wide range of alkenes. Its activity has been compared to the unsupported and Merrifield-supported **8** counterparts and the recyclability of both supported catalysts has also been investigated.

The Argogel-supported porphyrin **4** was prepared from Argogel chloride **2** (a PS-PEG copolymer) by our previously described synthetic procedure[14] (Scheme 1). The Merrifield-supported analogue **5**[15] was also synthesised using this novel procedure. 5-(4-Hydroxyphenyl)-10,15,20-triphenylporphyrin[16] **1** (deprotonated in situ with potassium carbonate) was attached to the chloride resins **2** (Argogel chloride) and **3** (Merrifield resin) via a covalent ether linkage.[17]



Scheme 1. Synthesis of Argogel-supported porphyrin **4** and Merrifield-supported porphyrin **5**.

Keywords: manganese porphyrin; support; Merrifield; epoxidation; recycling.

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0040-4039/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0040-4039(02)02063-4

In both cases, the reaction was performed in anhydrous DMF with catalytic potassium iodide for 3 days, in order to achieve complete displacement of the chloride. The yields of supported porphyrin, based on nitrogen microanalysis,[17] were 75% for the Argogel porphyrin (AG-TPP) **4** (after three treatments) and 93% for the Merrifield porphyrin (MR-TPP) **5** (after a single treatment). The supported porphyrins **4** and **5** were also characterised by Gel Phase High Resolution Magic Angle Spinning (HR-MAS) ^{1}H NMR and Single Bead FT-IR spectroscopy.

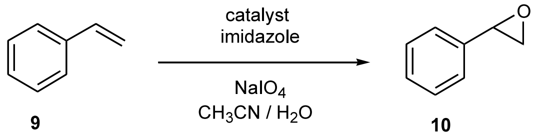
The supported porphyrins **4** and **5** were then metallated using manganese dichloride **6** (Scheme 2) in refluxing DMF under rigorously anaerobic conditions.[18] The yields obtained for this step were quantitative for the Argogel-supported manganese porphyrin **7** (AG-TPPMnCl) and for the Merrifield-supported manganese porphyrin **8** (MR-TPPMnCl). Catalyst loadings were calculated from the manganese content determined by ICP-AES (0.28 mmol g^{-1} for **7**, 0.52 mmol g^{-1} for **8**). SEM analysis of the catalyst beads confirmed that spherical morphology had remained intact, while X-EDS proved the presence of manganese and chlorine within the beads.

Following the successful synthesis of the two supported metalloporphyrins bearing different spacer chains, their catalytic activity was initially tested in the epoxidation of styrene **9** (Scheme 3). The catalytic assay[12] involved the use of sodium periodate ($NaIO_4$) as the oxidant and imidazole as the axial ligand for the metalloporphyrin. The activity of the supported catalysts **7** and **8** was compared to a simple soluble manganese tetraphenylporphyrin (TPPMnCl) catalyst (Table 1).

This epoxidation reaction was monitored by gas chromatography (GC) and styrene oxide **10** was found to be the major product in all cases, but by-products[†] were also detected in a much lower yield and identified by GC–MS. The yield of styrene oxide **10** (80–86%) was high in all cases[‡] (Table 1). The highest yield was obtained for the MR-TPPMnCl catalyst **8**.

For the novel AG-TPPMnCl catalyst **7**, the investigation was extended to the epoxidation of different aromatic and aliphatic alkenes. Two different catalytic assays involving two different solvent mixtures (CH_3CN/H_2O[12] or CH_2Cl_2/H_2O[19]) were used depending on the solubility of the alkenes. The results obtained are shown in Table 2.[§]

The Argogel-supported manganese porphyrin **7** (AG-TPPMnCl) led to good yields (51–90%) for the epoxidation of aromatics alkenes (entries 1–3). In the case of aliphatic alkenes (entries 3–8), the highest yields were obtained for the formation of epoxycyclooctane and epoxycyclohexane (98 and 90%, respectively) (entries 4–5) whereas linear alkenes such as 1-hexene and 1-

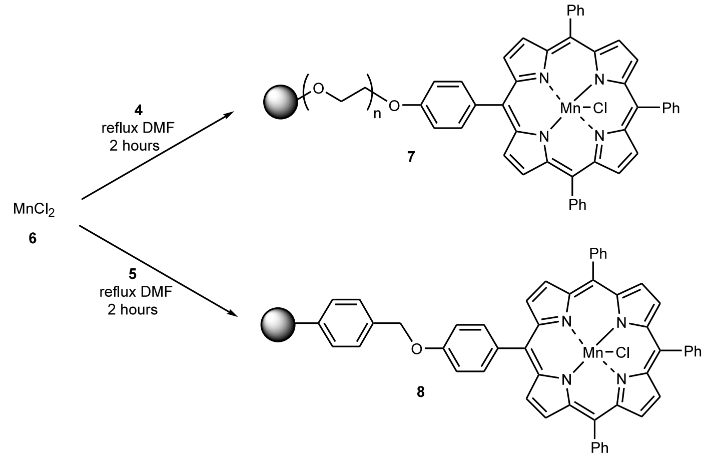


Scheme 3. Epoxidation of styrene **9** using $NaIO_4$ as the oxidant.

Table 1. Styrene epoxidation using $NaIO_4$ as the oxidant after 12 h

Catalyst	Yield epoxide (%)[a]
TPPMnCl	80[b]
AG-TPPMnCl **7**	80[b]
MR-TPPMnCl **8**	86[b]

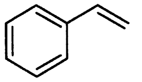
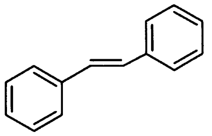
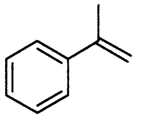
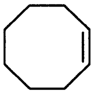
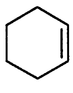
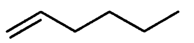
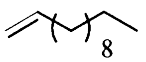
[a] Determined by GC (based on starting material and by-products).
[b] Conditions: catalyst:imidazole:alkene:$NaIO_4$ (1 mmol in 2.7 mL of H_2O) molar ratio of 1:10:23:46, $CH_3CN:H_2O$ 2:1.



Scheme 2. Synthesis of Argogel-supported catalyst **7** and Merrifield-supported catalyst **8**.

[†] Benzaldehyde and phenylacetaldehyde.
[‡] Control experiments carried out without catalyst did not lead to formation of any products.

Table 2. Olefin epoxidation using AG-TPPMnCl **7** and $NaIO_4$ as the oxidant after 12 h

Entry	Alkene	Yield epoxide[a] (%)
1	 b	80
2	 c	90
3	 b	51
4	 b	98
5	 b	90
6	 b	64
7	 d	24
8	 d	22

[a] Determined by GC (based on starting material consumed and by-products present).

[b] Conditions: AG-TPPMnCl:imidazole:alkene:$NaIO_4$ (1 mmol in 2.7 mL of H_2O) molar ratio of 1:10:23:46, CH_3CN:H_2O 2:1.

[c] AG-TPPMnCl:imidazole:alkene:PTC[§]:$NaIO_4$ (1.4 mmol in 10 mL of H_2O) molar ratio of 1:10:83:10:167, CH_2Cl_2:H_2O 1:5.

[d] AG-TPPMnCl:imidazole:alkene:PTC[§]:$NaIO_4$ (1 mmol in 10 mL of H_2O) molar ratio of 1:10:100:10:230, CH_2Cl_2:H_2O 1:5.

dodecene (entries 7–8) led to poorer results (ca. 20% yield). The yields obtained are in agreement with previously reported results for soluble metalloporphyrin catalysts.[19]

The recovery and recyclability of the Argogel and Merrifield supported manganese porphyrins **7** and **8** have also been examined. The catalysts were tested for activity in the epoxidation of styrene. After each reaction, the catalyst beads were filtered, washed and dried, then examined by ICP-AES to determine the catalyst loading (from %Mn analysis). The solution was also examined by UV spectroscopy in order to establish whether any manganese porphyrin had leached from the resin during the reaction. The catalyst beads were then reused and it was found that the recycled Argogel-bound catalyst **7** suffered a dramatic decrease in activity after three cycles (cycle 1: 80%, cycle 2: 60%, cycle 3: 3%). This drop in activity was attributed to cleavage of the PEG chain since the UV analysis of the solution proved the presence of manganese porphyrin, while ICP-AES analysis showed a decrease in manganese content within the beads. However, the recyclability of the Merrifield-supported catalyst **8** under the same conditions was successfully achieved (Table 3). After three

Table 3. Recyclability of MR-TPPMnCl **8** for styrene epoxidation after 12 h

Cycle	Yield epoxide (%)[a] using MR-TPPMnCl **8**[b]
1	86
2	85
3	75

[a] Determined by GC (based on starting material and by-products).

[b] Conditions: MR-TPPMnCl:imidazole:alkene:$NaIO_4$ (1 mmol in 2.7 mL of H_2O) molar ratio of 1:10:23:46, CH_3CN:H_2O 2:1.

[§] PTC: Phase transfer catalyst (benzyldimethyl tetradecylammonium chloride dihydrate.

cycles, only a small decrease in activity (from 86% to 75%) was observed, and moreover, no manganese porphyrin was detected in the solution when analysed by UV spectroscopy.

In conclusion, we have developed a new efficient route to supported manganese porphyrins, and demonstrated the effectiveness of Argogel and Merrifield-bound catalysts **7** and **8** as alkene epoxidation catalysts. Detailed studies have shown that Merrifield resin is a superior support for this catalyst, as it can be recycled with minimum loss of activity.

Acknowledgements

We thank King's College London for financial support (E. Brulé), and the Royal Society (Dorothy Hodgkin Fellowship to Y. R. de Miguel).

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18. AG-TPP **4** or MR-TPP **5** was placed in a flask equipped with an overhead stirrer under N_2. Anhydrous DMF was added and the reaction mixture was refluxed at 158°C for 5 min and manganese dichloride (100 equiv.) was added under N_2. The mixture was then stirred at 60 rpm in refluxing DMF for 2.5 h. After cooling to room temperature, the beads were washed with water, acetone, DCM and HPLC-grade pentane and dried under vacuum. Manganese analysis (ICP-AES) showed 100% metallation in both cases (1.54% Mn, loading of 0.28 mmol g^{-1} for AG-TPPMnCl **7** and 2.86% Mn, loading of 0.52 mmol g^{-1} for MR-TPPMnCl **8**).
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