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# Rapid and highly selective epoxidation of alkenes by tetrabutylammonium monopersulfate in the presence of manganese *meso*-tetrakis(pentafluorophenyl)porphyrin and tetrabutylammonium salts or imidazole co-catalysts

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**Abstract**—Epoxidation of various alkenes in low to high yields (29–100%) and good to excellent selectivities (75–100%) was performed with tetrabutylammonium monopersulfate in the presence of *meso*-tetrakis(pentafluorophenyl)porphyrin as catalyst and tetrabutylammonium acetate or fluoride or imidazole as co-catalysts in $CH_2Cl_2$, in less than 10 min at room temperature (~25 °C).


Biomimetic epoxidation of alkenes has been achieved using various synthetic manganese(III) porphyrins in association with oxidants, such as PhIO,[1] NaOCl,[2] $H_2O_2$,[3] periodate,[4] and *n*-$Bu_4NHSO_5$.[5] It was found that the rates and selectivities of these reactions are critically dependent upon the use of nitrogen donor co-catalysts.[3a,6] Also, it has been demonstrated that, instead of nitrogen donors, ammonium acetate can be employed as an effective co-catalyst.[7] Contrary to the oxidative degradation of the nitrogen donors,[8] salt co-catalysts are quite stable under these oxidizing conditions.[9]

In this work we describe for the first time the epoxidation of alkenes in low to high yields and good to excellent selectivities, in very short times using *n*-$Bu_4NHSO_5$[10] in the presence of MnTPFPP(OAc)[11] catalyst in association with either *n*-$Bu_4NOAc$[12] and *n*-$Bu_4NF$ or imidazole co-catalysts, Tables 1 and 2. The results obtained clearly show how the relative reactivities of the aryl alkenes versus cyclooctene, cyclohexene, and 1-octene differ substantially in accord with the nature of the co-catalysts, under similar conditions, Table 2.

The general procedure for oxidation consisted of adding *n*-$Bu_4NHSO_5$ (0.19 mmol) to a $CH_2Cl_2$ (0.5 mL) solution containing the alkene (0.1 mmol), MnTPFPP(OAc) (0.001 mmol) and tetrabutylammonium salts[12] or imidazole (ImH) as co-catalysts (0.04 or 0.02 mmol). The solutions were stirred at a constant speed, under air, at room temperature. The consumption of the starting alkene and formation of epoxide were monitored by GLC and $^1H$ NMR.

The results of epoxidations of a series of alkenes in the presence of MnTPFPP(OAc) as catalyst and two different salt co-catalysts, *n*-$Bu_4NOAc$ and *n*-$Bu_4NF$, are given in Table 1. Considering the reaction times, *n*-$Bu_4NOAc$ is clearly a more effective co-catalyst than *n*-$Bu_4NF$ (entries 1–10). However, the selectivities were very similar.

To compare both the relative reactivities of alkenes and also the co-catalytic properties of *n*-$Bu_4NOAc$ with ImH, we carried out similar epoxidation reactions with the same catalyst–co-catalyst–substrate–oxidant ratios (1:20:100:190), in $CH_2Cl_2$, for 1 min, Table 2. It was observed that the relative reactivities of alkenes were quite different for *n*-$Bu_4NOAc$ and ImH co-catalysts, except for *trans*-β-methylstyrene. It was shown that the selectivities of epoxidation of alkenes were very similar except for α-methylstyrene and 3-Cl-styrene (entries 2 and 5), for which ImH was a more selective co-catalyst.

*Keywords*: Epoxidation; Tetrabutylammonium monopersulfate; Manganese porphyrin; Tetrabutylammonium salt; Co-catalyst.
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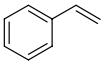
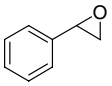
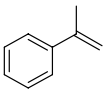
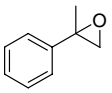
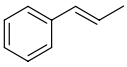
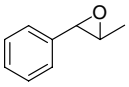
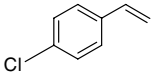
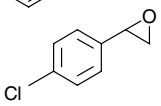
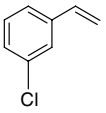
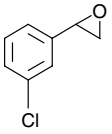
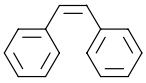
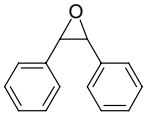
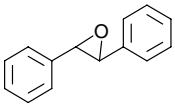
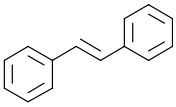
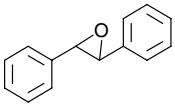
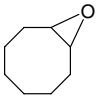
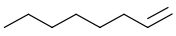
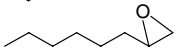
**Table 1.** Epoxidation of alkenes with *n*-$Bu_4NHSO_5$ catalyzed by MnTPFPP(OAc) in the presence of *n*-$Bu_4NOAc$ or *n*-$Bu_4NF$ in $CH_2Cl_2$[a]

| Entry | Alkene | Conversion[b] (%) | Epoxide | Epoxide yield[b] (%) | Selectivity[b] (%) | Time (min) |
|---|---|---|---|---|---|---|
| 1 |  | 98 (91)[c] |  | 76 (72)[c] | 78 (79)[c] | 1 (2)[c] |
| 2 |  | 90 (98)[c] |  | 78 (86)[c] [70][e] | 87 (88)[c] | 1 (7)[c] |
| 3 |  | 98 (79)[c] |  | 98 (79)[c] [83][e] | 100 (100)[c] | 8 (10)[c] |
| 4 |  | 98 (97)[c] |  | 96 (88)[c] [89][e] | 98 (91)[c] | 1 (3)[c] |
| 5 |  | 96 (98)[c] |  | 88 (85)[c] [80][e] | 92 (87)[c] | 1 (5)[c] |
| 6 |  | 98 (96[c]) |  | 92 (92)[c,d] | 94 (96)[c] | 1 (5[c]) |
| | | |  | 6 (4)[c,d] | 6 (4)[c] | |
| 7 |  | 73 (50)[c] |  | 73 (50)[c,d] | 100 (100)[c] | 10 (10)[c] |
| 8 |  | 95 (97)[c] |  | 93 (95)[c] | 98 (98)[c] | 2 (8)[c] |
| 9 |  | 93 (90)[c] |  | 91 (88)[c] [80][e] | 98 (98)[c] | 5 (10)[c] |
| 10 |  | 79 (29)[c] |  | 77 (28)[c] | 97 (97)[c] | 10 (10)[c] |

[a] Reactions were run at least in triplicate under air at 25 ± 2 °C, and the reported values are the average of the measured values. The molar ratio for catalyst–co-catalyst–substrate–oxidant is 1:40:100:190.

[b] The GC conversions (%) to the products and the epoxide yields (%) were measured relative to the starting alkenes. The conversion % is defined as [(the number of moles of the starting alkene converted to the product(s))/(the number of moles of the starting alkene)] × 100; epoxide yield % is equal to [(the number of moles of the epoxide obtained)/(the number of moles of the starting alkene)] × 100. The epoxide selectivity % is [(the number of moles of the epoxide formed)/(the number of moles of the starting alkene converted to the product(s))] × 100.

[c] The data outside the parentheses are for *n*-$Bu_4NOAc$ and those in the parentheses correspond to *n*-$Bu_4NF$.

[d] The organic product(s) and the unreacted alkenes were separated by silica gel chromatography and the isomer ratios were determined by $^1H$ NMR spectroscopy.

[e] The isolated pure epoxides were obtained in the presence of *n*-$Bu_4NOAc$.[13]

Also, the epoxidation of *cis*-stilbene proceeded with a lower stereospecificity in the presence of *n*-$Bu_4NOAc$ (93%) than ImH (100%). Alkenes with potential π-donor aryl substituents (entries 1–7), were generally much more reactive (conversion %, 27–98) than cyclohexene, cyclooctene, and 1-octene (conversion %, 17–52) (entries 8–10), in the presence of *n*-$Bu_4NOAc$. Whereas this order was virtually reversed when ImH co-catalyst was used, and the relatively less hindered cyclohexene, cyclooctene, and 1-octene displayed greater or similar reactivities (conversion %, 49–62) as compared to the aryl alkenes (conversion %, 38–56). The less hindered monosubstituted styrene and 4-Cl-styrene were distinctly more reactive than disubstituted styrenes (entries 2, 3, 6, and 7), and 3-Cl-styrene, using *n*-$Bu_4NOAc$, Table 2.

The differing results obtained using *n*-$Bu_4NOAc$ versus ImH clearly indicate that the active oxidizing species for these co-catalysts may be very different. Addition

**Table 2.** Epoxidation of alkenes with *n*-$Bu_4NHSO_5$ catalyzed by MnTPFPP(OAc) in the presence of *n*-$Bu_4NOAc$ or ImH in $CH_2Cl_2$[a]

| Entry | Alkene | Conversion[b] (%) | Epoxide yield [b] (%) | Selectivity (%) |
|---|---|---|---|---|
| 1 | Styrene | 98 (41)[c] | 76 (33)[c] | 78 (80)[c] |
| 2 | α-Methylstyrene | 88 (56)[c] | 75 (56)[c] | 85 (100)[c] |
| 3 | *trans*-β-Methylstyrene | 52 (50)[c] | 51 (50)[c] *trans* | 98 (100)[c] |
| 4 | 4-Cl-Styrene | 95 (46)[c] | 92 (44)[c] | 97 (96)[c] |
| 5 | 3-Cl-Styrene | 83 (38)[c] | 77 (37)[c] | 93 (97)[c] |
| 6 | *cis*-Stilbene | 89 (40[c]) | 83 (40)[c,d] *cis* | 93 (100)[c] |
| | | | 6 (trace)[c,d] *trans* | 7 |
| 7 | *trans*-Stilbene | 27 (18)[c] | 27 (18)[c,d] *trans* | 100 (100)[c] |
| 8 | Cyclooctene | 52 (62)[c] | 50 (62)[c] | 96 (100)[c] |
| 9 | Cyclohexene | 20 (52)[c] | 19 (52)[c] | 95 (100)[c] |
| 10 | 1-Octene | 17 (49)[c] | 17 (48)[c] | 98 (98)[c] |

[a] All the reaction conditions were the same as those described in Table 1 except for a different catalyst–co-catalyst ratio (1:20), and the reaction time (1 min).

[b] The GC conversions (%) or epoxide yields (%) were measured relative to the starting alkenes.

[c] The data outside of the parentheses refer to *n*-$Bu_4NOAc$ co-catalyst and those inside the parentheses relate to ImH.

[d] The organic product(s) and the unreacted alkenes were separated by silica gel chromatography and the isomer ratios were determined by $^1H$ NMR spectroscopy.

of ImH ($2.4\times10^{-4}$ mmol) and then *n*-$Bu_4NHSO_5$ ($2.3\times10^{-3}$ mmol) to a solution of MnTPFPP(OAc) ($1.2\times10^{-5}$ mmol) in $CH_2Cl_2$ (2 mL) (Soret, $\lambda_{max}=474$ nm) had virtually no effect on the Soret band position. In contrast, addition of *n*-$Bu_4NOAc$ ($2.4\times10^{-4}$ mmol) to a $CH_2Cl_2$ solution of MnTPFPP(OAc) ($1.2\times10^{-5}$ mmol) very rapidly (<15 s) produced a new intense Soret band ($\lambda_{max}=466$ nm), presumably due to the formation of a six-coordinate [MnTPFPP-$(OAc)_2$]-species. By adding *n*-$Bu_4NHSO_5$ ($2.3\times10^{-3}$ mmol) to this solution, the Soret band at $\lambda_{max}=466$ nm gradually disappeared (500 s), and concomitantly a Soret band at $\lambda_{max}=418$ nm, probably corresponding to an Mn-oxo species,[14] increased to a maximum. Addition of a large excess of alkene again gave the original Soret band ($\lambda_{max}=466$ nm). Accordingly, it seems plausible to conclude that for *n*-$Bu_4NOAc$ co-catalyst, an MnTPFPP(OAc)(O) species is the primary active oxidant, whereas in the case of ImH the functional oxidant is predominantly the six-coordinate MnTPFPP(ImH)-$(HSO_5)$ complex. Consideration of the steric properties of the alkenes (see above) suggests that steric hindrance operating at the oxygenation site of MnTPFPP-(OAc)(O) must be greater than that of MnTPFPP(ImH)-$(HSO_5)$. It seems that the strong withdrawal of the Mn-oxo group, with its short bond length, into the cavity of the *meso*-tetrakis(pentafluorophenyl) groups of the porphyrin, by the *trans* $OAc^-$ axial ligand, might be the main cause of the observed larger steric hindrance of the former than the latter.[14]

Examination of the co-catalytic properties of a variety of *n*-tetrabutylammonium salts,[12] in the epoxidation of α-methylstyrene demonstrates that the acetate and fluoride salts are the best co-catalysts, considering a combination of both conversion % and selectivity %, Table 3. However, *n*-$Bu_4NSCN$ appears to be an excellent co-catalyst, in terms of selectivity of the epoxidation.

Comparison of catalytic activities of four different MnPor(OAc) species, for epoxidation of styrene in the presence of both *n*-$Bu_4NOAc$ and *n*-$Bu_4NF$ co-catalysts,

**Table 3.** Epoxidation of α-methylstyrene with *n*-$Bu_4NHSO_5$ catalyzed by MnTPFPP(OAc) in the presence of various tetrabutylammonium salts in $CH_2Cl_2$[a]

| Salt | Conversion[b] (%) | Epoxide yield[b] (%) | Selectivity (%) | Time (min) |
|---|---|---|---|---|
| *n*-$Bu_4NOAc$ | 88 | 74 | 84 | 1 |
| *n*-$Bu_4NF$ | 67 | 58 | 86 | 10 |
| *n*-$Bu_4NCl$ | 62 | 42 | 68 | 10 |
| *n*-$Bu_4NBr$ | 79 | 28 | 35 | 10 |
| *n*-$Bu_4NN_3$ | 61 | 41 | 67 | 10 |
| *n*-$Bu_4NOCN$ | 58 | 33 | 57 | 10 |
| *n*-$Bu_4NSCN$ | 31 | 28 | 90 | 10 |
| $(n\text{-}Bu_4N)_2SO_4$ | 64 | 44 | 69 | 10 |
| *n*-$Bu_4NHSO_4$ | 9 | 5 | 55 | 10 |
| *n*-$Bu_4NNO_3$ | 3 | 1 | 33 | 10 |
| None | — | — | — | 10 |

[a] Reactions were run at least in triplicate under air at 25 ± 2 °C, and the reported data represent the average values. The molar ratio for catalyst–co-catalyst–substrate–oxidant is 1:20:100:190.

[b] The GC conversions (%) and epoxide yields (%) were measured relative to the starting alkene.

under similar conditions, shows that MnTPFPP(OAc) is the best catalyst among this series, Table 4. The lower catalytic properties of MnTMP(OAc)[11] and MnTDCPP(OAc)[11] in comparison to MnTPFPP(OAc) can be related to their larger steric hindrance. Whereas, the lower catalytic activity of MnTPP(OAc)[11] than MnTPFPP(OAc) reflects the lower stability of the former than the latter toward oxidative degradation. This contrasts the behavior of MnTPP(OAc) as an oxidation catalyst in the presence of ImH co-catalyst.[5d] It should be noted that with molar ratios of 20000:1:2500:36000 for styrene–MnTPFPP(OAc)–*n*-$Bu_4NOAc$–*n*-$Bu_4NHSO_5$ a total turnover number of 13,000 was achieved for epoxidation of styrene, in $CH_2Cl_2$, in 72 h, at room temperature.

In conclusion, this work shows that epoxidation of alkenes in low to high yields and good to excellent selectivities can be performed with *n*-$Bu_4NHSO_5$ in the presence of MnTPFPP(OAc) catalyst in association with *n*-$Bu_4NOAc$, *n*-$Bu_4NF$, or ImH co-catalysts, in $CH_2Cl_2$, at

**Table 4.** Catalytic activities of various MnPor(OAc) species for epoxidation of styrene in the presence of *n*-$Bu_4NOAc$ and *n*-$Bu_4NF$ salts[a]

| Salts | MnPor(OAc) | | | |
|---|---|---|---|---|
| | TPP | TMP | TDCPP | TPFPP |
| *n*-$Bu_4NOAc$ | 19 | 5 | 10 | 98[b] |
| *n*-$Bu_4NF$ | 14 | 2 | 2 | 91[c] |

[a] The molar ratios for catalyst–co-catalyst–substrate–oxidant and the general reaction conditions are the same as those for Table 1, with 10 min reaction times.
[b] 1 min reaction time.
[c] 2 min reaction time.

room temperature. The very high stability of *n*-tetrabutylammonium salt co-catalysts and moderate stability of MnTPFPP(OAc) catalyst toward oxidative degradation would seem to make these catalytic systems very suitable for achieving high turnover numbers for epoxidation of alkenes.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.07.119.

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10. The synthesis of *n*-$Bu_4NHSO_5$ was based on the procedures given by: Compestrini, S.; Meunier, B. *Inorg. Chem.* **1992**, *31*, 1999–2006, and Ref. 5d. Freshly prepared *n*-$Bu_4NHSO_5$ was a much stronger oxidant than commercially available samples. Since the oxidizing ability of *n*-$Bu_4NHSO_5$ samples reduces with time, in order to obtain reproducible results, the *freshly* prepared oxidant was refrigerated and used within three days. *Caution*: *n*-$Bu_4NHSO_5$ should be considered as a potential explosive.
11. The free base porphyrins and MnPor(OAc) were synthesized by standard methods: $TPFPPH_2$ = *meso*-tetrakis-(pentafluorophenyl)porphyrin (Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827–836); $TPPH_2$ = *meso*-tetraphenylporphyrin (Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476); $TMPH_2$ = *meso*-tetrakis(2,4,6-trimethylphenyl)porphyrin and $TDCPPH_2$ = *meso*-tetrakis(2,6-dichlorophenyl)porphyrin (Hoffman, P.; Robert, A.; Meunier, B. *Bull. Soc. Chim. Fr.* **1992**, *129*, 85–97); MnTPFPP(OAc) (Kadish, K. M.; Araullo-McAdams, C.; Han, B. C.; Franzen, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 8364–8368); MnTPP(OAc), MnTMP(OAc), and MnTDCPP(OAc) (Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443–2445).
12. (a) *n*-$Bu_4NOAc$ was prepared by adding tetrabutylammonium hydrogen sulfate (6.5 mmol) to a solution of sodium acetate (32.5 mmol) in water (40 mL). The mixture was stirred for 30 min and then extracted with $CH_2Cl_2$ (80 mL) and the extract dried over magnesium sulfate. After filtration and evaporation of the solvent, the remaining paste was washed with hexane (10 mL) and dried under vacuum. Other tetrabutylammonium salts were prepared by exchanging $Br^-$ in *n*-$Bu_4NBr$ with other anions by a similar procedure to the above. (b) *n*-$Bu_4NF{\cdot}3H_2O$ and *n*-$Bu_4NBr$ were purchased from Fluka.
13. A mixture of the alkene (1 mmol), MnTPFPP(OAc) (0.01 mmol), *n*-$Bu_4NOAc$ (0.4 mmol), and *n*-$Bu_4NHSO_5$ (1.9 mmol) in $CH_2Cl_2$ (5 mL), was stirred for 30 min, and then the majority of the solvent was removed, at room temperature. For the aryl alkenes the epoxides were separated using preparative TLC (silica gel 60, $GF_{254}$, Merck, on a 20 cm × 20 cm plate) using *n*-hexane–ethyl acetate (7:1, v:v) as the mobile phase. For the separation of the cyclohexene oxide a silica gel column (silica gel 40, mesh 70–230, Fluka, in *n*-hexane), and *n*-hexane–ethyl acetate (7:1, v:v) eluent was used.
14. Rebelo, S. H.; Pereira, M. M.; Simões, M. M. Q.; Neves, M. G. M. S.; Cavaleiro, J. A. S. *J. Catal.* **2005**, *234*, 76–87.