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Sodium Periodate Epoxidation of Alkenes Catalysed by Manganese Porphyrins†

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Epoxidation of alkenes with different electronic and steric properties has been performed with high selectivity by sodium periodate in the presence of acetatotetraarylporphinatomanganese(III) complexes containing electron releasing or withdrawing groups at the *ortho* positions of the aryl rings, in a two-phase (CH_2Cl_2–H_2O) medium at 24 ± 2 °C.

Synthetic manganese porphyrins in association with different oxidants have provided effective model systems for mimicking the enzymatic role of cytochrome *P*-450 in the oxygenation of hydrocarbons.[1] The steric and electronic properties of substituents on the periphery of metalloporphyrins and also on alkenes strongly affect the selectivity and product distribution of oxygenations.[2] Recently, it has been shown that sodium periodate can efficiently epoxidize various alkenes in the presence of chlorotetraphenylporphinatomanganese(III).[3] In this report we wish to describe several alkene epoxidations by $NaIO_4$ in the presence of Mn-porphyrins with different steric and electronic properties.

In a typical reaction, to a solution of Mn(porphyrin)OAc (0.006 mmol) in CH_2Cl_2 (2 ml) tetra-*n*-butylammonium bromide (0.25 or 0.063 mmol) as the phase transfer catalyst (PTC), imidazole (0.06 mmol) and substrate (0.5 or 0.6 mmol) were successively added. A solution of $NaIO_4$ (1.0 or 1.4 mmol in 10 ml water) was then added to the resulting mixture and the two phases were stirred thoroughly for the required time at 24 ± 2 °C.

Table 1 gives the results of epoxidation of various alkenes with sodium periodate in the presence of imidazole and different manganese porphyrins. The selectivity for epoxidation of all the alkenes (except for 1-methylcyclohexene, ⩾64%) lies in the range 86–100%.

The conversions clearly demonstrate the influence of steric and electronic properties of both the alkenes and the Mn-porphyrin catalysts. The disubstituted electron-rich alkenes, α-methylstyrene and hex-2-ene, show greater reactivity than the monosubstituted styrene and hep-1-ene, with all the catalysts. Epoxidation of *cis*- and *trans*-stilbenes particularly reflects the importance of steric effects in these reactions. Sterically demanding *trans*-stilbene shows poorer reactivity than the *cis*-isomer. This effect is especially pronounced when the sterically hindered Mn(TMP)OAc and Mn(TDCPP)OAc catalysts are employed. While oxidation of *trans*-stilbene only yields the corresponding oxide, oxygenation of *cis*-stilbene with Mn(TPP)OAc results in a mixture of 85% *cis*- and 15% *trans*-stilbene oxides. It is interesting to note that both Mn(TMP)OAc and Mn(TDCPP)OAc complexes, with bulky substituents at the *ortho* positions of the aryl rings, lead to nearly a quantitative production of *cis*-stilbene oxide. It appears that the formation of the thermodynamically more stable *trans*-stilbene oxide, which requires a free rotation about the alkene C–C bond at some intermediate step,[4] is effectively inhibited in these cases. The electron-rich 1-methylcyclohexene is more reactive than cyclohexene when the oxidations are performed in the presence of the less hindered Mn(TPP)OAc complex. These results imply that the electronic effects are dominant in these reactions. However, in the oxidation with Mn(TMP)OAc the steric factors become quite prominent and 1-methylcyclohexene shows poorer reactivity than cyclohexene.

Table 1 Epoxidation of various alkenes with $NaIO_4$ catalysed by Mn-porphyrins[a]

	Mn(TPP)OAc[a]			Mn(TDCPP)OAc[a]			Mn(TMP)OAc[a]		
Substrate	Conv. (%)[b]	Epox. (%)[b]	Selec. (%)[c]	Conv. (%)[b]	Epox. (%)[b]	Selec. (%)[c]	Conv. (%)[b]	Epox. (%)[b]	Selec. (%)[c]
α-Methylstyrene	61	58.5	96	50	46	92	81	79	97
Styrene	46	44.5	97	41	39	95	60	59	98
cis-Hex-2-ene	25	25	100	48	48	100	43	43	100
Hept-1-ene	7	7	100	29	29	100	34	34	100
cis-Stilbene[d]	100	85 (*cis*)	85	95	90 (*cis*)	95	86	86 (*cis*)	100
		15 (*trans*)	15		5 (*trans*)	5			
trans-Stilbene[d]	80	77 (*trans*)	96	15	15 (*trans*)	100	12	12 (*trans*)	100
1-Methylcyclohexene	50	45	90	42	27	64	21	15	71
Cyclohexene	25	23.5	94	36	34	94	30	26	86

[a]Reactions were performed under air at 24 ± 2 °C, with a catalyst:imidazole:substrate:oxidant:PTC molar ratio of 1:10:100:230:10. Abbreviations used are TPP, *meso*-tetraphenylporphyrin dianion; TMP, *meso*-tetramesitylporphyrin dianion; TDCPP, *meso*-tetrakis(2,6-dichlorophenyl)porphyrin dianion. Reactions were analysed after 1 h for Mn(TPP)OAc and Mn(TMP)OAc, and after 8 h for Mn(TDCPP)OAc. Products were determined by ^1H NMR and/or by comparison of their GC retention times with those of authentic samples. [b]GLC conversions and epoxide yields are based on the starting substrates. [c]Epoxide selectivity is defined as: [epoxide yield(%)/conversion(%)] × 100. [d]Molar ratio catalyst:imidazole:substrate:oxidant:PTC is 1:10:83:167:10 [40 for Mn(TDCPP)OAc]. Reactions were analysed after 5 h for Mn(TPP)OAc, Mn(TMP)OAc, and after 24 h for Mn(TDCPP)OAc by ^1H NMR.

Table 2 gives the results of epoxidation of styrene with $NaIO_4$ in the presence and absence of imidazole with different Mn-porphyrin catalysts. Epoxidation by Mn(TDCPP)OAc, having eight electronegative Cl groups, is strongly dependent upon the presence of imidazole. This catalyst produced only 19% of styrene oxides in the absence of imidazole after 11 h, whereas 100% conversion was obtained in the presence of imidazole during the same period. This contrasts sharply with the behaviour of Mn(TMP)OAc and Mn(TPP)OAc catalysts. These complexes demonstrated much greater activity in the absence of

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Table 2 Effect of imidazole on the epoxidation of styrene[a]

	With imidazole		No imidazole	
Catalyst	Conv. (%)[b]	Epox. (%)[b]	Conv. (%)[b]	Epox. (%)[b]
Mn(TDCPP)OAc	100	100	19	19
Mn(TMP)OAc	55	55	100	100
Mn(TPP)OAc	40	39	56	48

[a]Reactions were analysed after 75 min for Mn(TPP)OAc, Mn(TMP)OAc, and after 11 h for Mn(TDCPP)OAc. Similar molar ratio to (*d*) in Table 1 were employed. [b]GLC conversions and epoxide yields are based on the starting substrates.

imidazole. Complete epoxidation of styrene occurred within 75 min with Mn(TMP)OAc in the absence of imidazole, whereas under the same conditions and reaction time, but with imidazole, only 55% conversion was observed. The same general trend was also seen for Mn(TPP)OAc.

Interaction of Mn(TPP)OAc (Soret $\lambda_{max} = 479$ nm) with $NaIO_4$, under the oxidizing conditions employed, results in a blue-shift in its visible spectrum which clearly corresponds to the formation of a high-valent manganese species (Soret $\lambda_{max} = 401$ nm),[5] at ~24 °C. Fig. 1 shows the visible spectral changes caused by the addition of styrene to a CH_2Cl_2 solution of this highly active oxidant, and the reformation of Im-Mn(TPP)$^+$ species. Observation of isosbestic points at 381, 456, 493, 570 and 636 nm provides further evidence for this viewpoint.[6] Treatment of Mn(TMP)OAc (Soret $\lambda_{max} = 476$ nm) with $NaIO_4$ led to similar spectral changes and the formation of the related high-valent manganese complex (Soret $\lambda_{max} = 407$ nm). However, no such transformations were observed for Mn(TDCPP)OAc. It should be noted that the presence of imidazole seems to be necessary for the observation of the high-valent manganese species.[7]

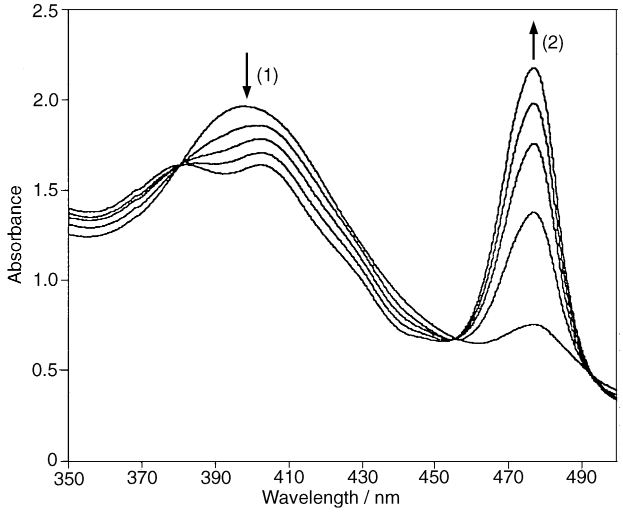

Fig. 1 Change in electronic absorption spectrum from that of a high-valent manganese species (**1**) to Im-Mn(TPP)$^+$ (**2**) in CH_2Cl_2

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