Use of an Oxaziridine as an Oxene Transfer Agent to Manganese(III) Tetraphenylporphyrin Chloride

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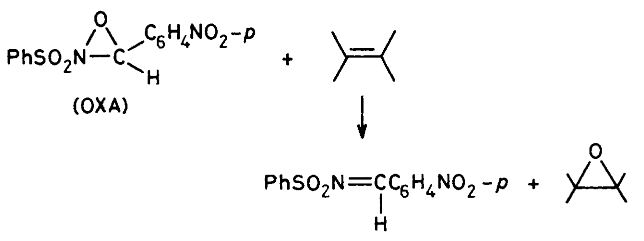
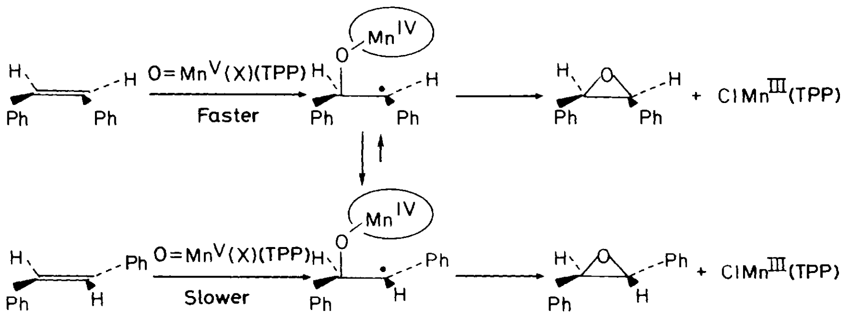
The oxaziridine OXA [2-phenylsulphonyl-3-(*p*-nitrophenyl)oxaziridine] is shown to be an effective oxene equivalent transfer agent to (tetraphenylporphinato)manganese(III) [ClMn^{III}(TPP)] allowing ClMn^{III}(TPP) catalysis of the oxidation of hydrocarbons by OXA.

The finding by Groves and co-workers[1] in 1979 that iodosylbenzene transfers an 'oxene' equivalent to iron(III) tetraphenylporphyrin salts initiated investigations on the use of a variety of oxidizing agents to generate porphyrin-bound higher valent state iron oxo and manganese oxo species. These reagents include percarboxylic acids,[2] hydroperoxides,[3] hypochlorite,[4] and *N,N*-dimethylaniline *N*-oxides,[5] and their use has extended our understanding of the chemistry of oxygen atom transfer to porphyrin-bound metal salts. The 2-sulphonyloxaziridines [including 2-phenylsulphonyl-3-(*p*-nitrophenyl)oxaziridine, OXA] were prepared and introduced as oxidizing agents by Davis and co-workers.[6,7] We now describe preliminary results (Table 1) of a study using manganese(III) tetraphenylporphyrin chloride [ClMn^{III}-(TPP)] as a catalyst for hydrocarbon oxidations by OXA. The concentration of ClMn^{III}(TPP) used was 8.0×10^{-4} M and product yields are reported at *ca.* $t_{1/2}$. Spectrophotometric examination of the reaction solutions at completion showed that [ClMn^{III}(TPP)] was unchanged.



Scheme 1

Inspection of Table 1 shows that ClMn^{III}(TPP) is an effective catalyst for epoxidation of alkenes by OXA. That the yield of epoxide with 2,3-dimethylbut-2-ene is 100% in the presence or absence of ClMn^{III}(TPP) (Scheme 1) reflects the fact that OXA is a good epoxidizing agent for this electron-rich alkene. However, OXA is unreactive with terminal olefins[7] and a rather poor epoxidizing agent for dialkyl substituted alkenes. In these instances ClMn^{III}(TPP) is an effective catalyst. Cyclohexene is converted into cyclohexene oxide with less than 1% formation of cyclohex-2-enol and cyclohex-2-enone. A similar result was observed with XMn^{III}-(TPP) (X = halogen) catalysts using *p*-cyano-*N,N*-dimethylaniline *N*-oxide as an oxygen source.[5e] When XFe^{III}-(TPP) is used with PhIO at least 10% of cyclohex-2-enol and/or cyclohex-2-enone are formed.[1,5b] Under vigorous conditions OXA alone has been reported to react stereo-



Scheme 2

Table 1. Hydrocarbon oxidation using OXA–$\mathrm{ClMn^{III}(TPP)}$ (at 25 °C, $\mathrm{CH_2Cl_2}$, $\mathrm{N_2}$ atmosphere).

Hydrocarbon, R	Ratio [R] : [OXA] : [$\mathrm{ClMn^{III}(TPP)}$]	Reaction time/h	% Yield[a] of epoxide
$\mathrm{Me_2C{=}CMe_2}$	10 : 5 : 1	2	100(100)
Bicyclo[2.2.1]hept-2-ene	25 : 5 : 1	2	40(2)
Cyclohexene	100 : 5 : 1	2	36(6)
	25 : 5 : 1	3	28(3)
Oct-1-ene	1000 : 5 : 1	3	26(1)
	25 : 5 : 1	3	5(0)
2-Methylhex-1-ene	25 : 5 : 1	3	15(2)
trans-Stilbene	100 : 5 : 1	3.8	23(4)
	25 : 5 : 1	4.4	8(1)
cis-Stilbene	100 : 5 : 1	5	*trans* 36(0) *cis* 46(0)
	25 : 5 : 1	4.6	*trans* 32(0) *cis* 39(0)
Cyclohexane	1000 : 10 : 1	18	Cyclohexanol[b] 10(0)
	25 : 5 : 1	17	1(0)

[a] % Yields are based on [OXA] added. Yields obtained in the absence of $\mathrm{ClMn^{III}(TPP)}$ are given in parentheses. The reactions were followed by g.c. analysis using a 25 m capillary column (Varian, WCOT, Vit. Silica) or in the case of the stilbenes by analysis using an Ultrasphere-Octyl column eluting with $\mathrm{MeOH{-}H_2O}$ (70 : 30 v/v). [b] *Ca.* 1% yields of cyclohex-2-enol and cyclohex-2-enone were obtained in the presence of $\mathrm{ClMn^{III}(TPP)}$.

specifically by *syn*-epoxidation of both *cis*- and *trans*-stilbenes.[7] With $\mathrm{ClMn^{III}(TPP)}$ as catalyst *trans*-stilbene produced only *trans*-stilbene oxide but *cis*-stilbene gave a mixture of *cis*- and *trans*-stilbene oxides in comparable yields (1.3 : 1). Similar results have been obtained with $\mathrm{(PhIOAc)_2 \cdot Mn^{IV}(TPP)}$ in chlorobenzene (1.7 : 1)[8] and $\mathrm{ClMn^{III}(TPP)}$ with PhIO in $\mathrm{CH_2Cl_2}$ (1.6 : 1).[9] These results show that an intermediate species is formed (see also refs. 4,9) which allows rotation about the C–C bond, and we propose the mechanism in Scheme 2. *trans*-Stilbene reacts slower than *cis*-stilbene because of steric hindrance to its approach to the porphyrin ring[9] but yields the most stable *trans*-intermediate and *trans*-epoxide. The more rapidly reacting *cis*-stilbene provides an intermediate with eclipsed phenyl substituents. Partial isomerization of this intermediate provides the more stable *trans*-conformation prior to oxirane formation (Scheme 2). Quasi-stable intermediate metalla-oxetanes, as proposed by Collman and collaborators,[4a,b] would then be formed by reversible ring closure of the intermediate radical species (Scheme 2). Benzaldehyde could not be detected with the stilbenes, as previously reported from stilbene oxidation with PhIO using $\mathrm{Cu^{II}}$ ion as a catalyst.[10] The yield of cyclohexanol obtained on hydroxylation of cyclohexane by OXA–$\mathrm{ClMn^{III}(TPP)}$ is comparable (10%) to that when PhIO–$\mathrm{ClFe^{III}(TPP)}$ is used (8%)[1] and better than with *p*-cyano-*N*,*N*-dimethylaniline *N*-oxide–$\mathrm{ClFe^{III}(TPP)}$ (2%).[5b]

The use of OXA with $\mathrm{ClMn^{III}(TPP)}$ possesses certain advantages over other metalloporphyrin based systems. Thus, with *m*-chloroperbenzoic acid and $\mathrm{XMn^{III}(TPP)}$ salts, the porphyrin catalyst undergoes preferential oxidation over cyclohexane.[11] Although hydroperoxides are quite ineffective with $\mathrm{XMn^{III}(TPP)}$ salts as epoxidizing and hydroxylating agents[3,11,12] iodosylbenzene serves as a good mono-oxygen donor molecule to $\mathrm{XMn^{III}(TPP)}$ and $\mathrm{XFe^{III}(TPP)}$ salts, but it exists in polymeric states and is quite insoluble. *p*-Cyano-*N*,*N*-dimethylaniline *N*-oxide (*p*-CNDMANO) is a preferred reagent for the kinetic study of 'oxene' transfer to metalloporphyrins because the porphyrin catalyst is not degraded. With *p*-CNDMANO, however, there is formed *p*-cyanodimethylaniline, which is itself a substrate and consumer of oxene equivalents, an unwanted feature in preparative reactions.[5] On the other hand OXA is stable, quite soluble in most useful solvents, and produces a stable sulphonimine on oxygen transfer. Unfortunately OXA is not a good oxygen transfer agent to $\mathrm{ClFe^{III}(TPP)}$.

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