Allylic oxidation and epoxidation of cycloalkenes by iodosylbenzene catalysed by iron(III) and manganese(III) tetra(dichlorophenyl)-porphyrin: the marked influence of ring size on the rate of allylic oxidation

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Five *cis*-cycloalkenes, with ring sizes 5, 6, 7, 8 and 10, and a *cis–trans* mixture of cyclododecene have been oxidised by iodosylbenzene using iron(III) or manganese(III) tetra(2,6-dichlorophenyl)porphyrin as catalysts. Both catalysts give very similar product distributions, although the reactions with the manganese porphyrin are sensitive to the presence of dioxygen whilst those with the iron porphyrin are not.

With all the substrates the dominant or sole reaction is epoxidation. However, with cyclopentene, cyclohexene and cyclododecene a significant amount of allylic oxidation also occurs. The dependence of the product distribution on the structure of the cycloalkene is discussed and attributed to the sensitivity of allylic oxidation rather than epoxidation to changes in ring size.

The active interest in hydrocarbon oxidation by cytochrome P450 dependent monooxygenases has been a major driving force behind the extensive studies of the intuitively simpler metalloporphyrin model systems.[1] Another has been the desire to explore and develop synthetic applications of these chemical models in selective oxidations.[1]

The most thoroughly investigated hydrocarbon oxidation has been alkene epoxidation. This research has provided a wealth of mechanistic information[2] and some potential routes to useful synthetic intermediates (*e.g.* enantioselective epoxidation).[3] A minor side reaction which can also occur in these reactions is allylic oxidation.[4] This arises from a competition of the allylic C–H and the C=C double bond of the alkene for the active oxidant (Scheme 1) and consequently the product distribution depends on the structure of the alkene and metalloporphyrin. With PhIO/Mn^{III}P or Fe^{III}P systems allylic oxidation is a minor pathway which is normally only detected with terminal or *trans*-dialkylalkenes.[4b,c,5] With these substrates, for steric or electronic reasons, the C=C bond is relatively unreactive towards epoxidation and this allows allylic oxidation to compete more effectively.[4,6]

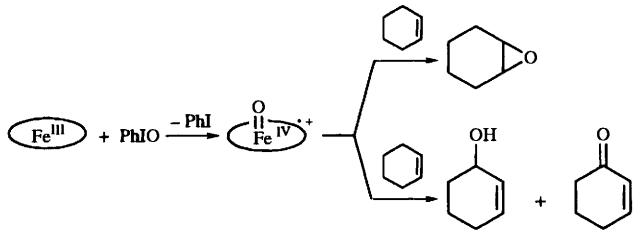
We and others have noted the marked difference in the metalloporphyrin-catalysed oxidations of cyclohexene and cyclooctene by iodosylbenzene.[6a,7] The former invariably lead to both epoxidation and allylic oxidation whereas the latter are cleanly selective for epoxidation.[4a,c,6a,7,8]

The influence of ring size on the rates of reaction of cycloalkyl systems is well documented and has been accounted for in terms of differences in strain and non-bonded interactions in the substrate and the rate-determining transition state.[9] In this paper we describe our studies on the metalloporphyrin-catalysed oxidation of a series of cycloalkenes. The results provide an insight into the factors that control allylic oxidation and epoxidation of alkenes in these systems and the origin of the markedly different behaviour of cyclohexene and cyclooctene.

Results

Oxidation systems

Two metalloporphyrins, iron(III) and manganese(III) tetra(2,6-dichlorophenyl)porphyrin (Fe^{III}TDCPP and Mn^{III}TDCPP) (Fig. 1) have been used to catalyse the oxidation of a selection of cycloalkenes by iodosylbenzene in dichloromethane. The



Scheme 1

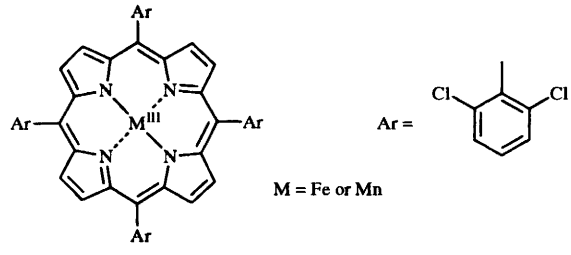


Fig. 1 Iron(III) and manganese(III) tetra(2,6-dichlorophenyl)porphyrin catalysts

molar proportions of catalyst:PhIO:alkene employed were 1:100:2000.

Product distributions

The product distributions and yields from the oxidations of cyclopentene, cyclohexene, cycloheptene, (*Z*)-cyclooctene, (*Z*)-cyclodecene and a mixture of (*Z*)- and (*E*)-cyclododecene were monitored (GC analysis) with time (*e.g.* Fig. 2). The final yields, typically after 30 min for the Fe^{III}TDCPP and after 30–60 min for the Mn^{III}TDCPP systems are recorded in Tables 1 and 2. The conversion of PhIO to alkene oxidation products was very good and the reproducibility of the reactions was excellent (±2%). Control reactions showed that in the absence of the metalloporphyrins no detectable oxidation of the substrates occurred within 60 min.

With both catalysts, cyclopentene, cyclohexene and the mixture of (*Z*)- and (*E*)-cyclododecene gave epoxide and significant yields of allylic oxidation products. In contrast, the reactions of cycloheptene, (*Z*)-cyclooctene and (*Z*)-cyclodecene, except that of cycloheptene with the Mn^{III}TDCPP system,

Table 1 Oxidation of cycloalkenes by iodosylbenzene in CH_2Cl_2 catalysed by $Fe^{III}TDCPP$[a]

Substrate	Conditions	Yield (%)[b] Epoxide	Allylic alcohol	Allylic ketone	Oxidant accountability (%) Alkene oxid. prod.[c]	PhI[b]
C_5H_8	Air	64	19	1.9	92	95
C_5H_8	N_2	65	19	0.7	89	96
C_6H_{10}	Air	65	7.5	2.7	90	86
C_6H_{10}	N_2	65	8.1	2.5	90	87
C_7H_{12}	Air	81	*d*	*d*	91	89
c-C_8H_{14}	Air	87	*d*	*d*	89	98
c-$C_{10}H_{18}$	Air	66	*d*	*d*	97	69
$C_{12}H_{22}$[e]	Air	69[f]	0.7[g]	5[g]	101	79

[a] Conditions: $Fe^{III}TDCPP$ (5×10^{-8} mol), PhIO (5×10^{-6} mol), cycloalkene (1×10^{-4} mol) in CH_2Cl_2 (3 cm^3), reaction time 30 min. [b] Based on PhIO. [c] Conversion of PhIO into epoxide and allylic oxidation products. It is assumed that the formation of ketone consumes two molecules of PhIO. [d] < 0.1%. [e] 36:64 mixture of *cis*- and *trans*-alkenes. [f] *cis*- + *trans*-Epoxide, in the proportions 65:35. [g] Detected by GC–MS.

Table 2 Oxidation of cycloalkenes by iodosylbenzene in CH_2Cl_2 catalysed by $Mn^{III}TDCPP$[a]

Substrate	Conditions	Yield (%)[b] Epoxide	Allylic alcohol	Allylic ketone	Oxidant accountability (%) Alkene oxid. prod.[c]	PhI[b]
C_5H_8	Air	78	8	17	137 (118)[d]	87
C_6H_{10}	Air	84	15	17	156 (136)[d]	85
C_6H_{10}	Argon	53	6	2	85 (82)[d]	74
C_7H_{12}	Air	87	*e*	*e*	96	91
c-C_8H_{14}	Air	79	*f*	*f*	91	86
c-$C_{10}H_{18}$	Air	85	*f*	*f*	96	89
$C_{12}H_{22}$[g]	Air	58[h]	6[i]	11[i]	103 (90)	83

[a] Conditions: $Mn^{III}TDCPP$ (5×10^{-8} mol), PhIO (5×10^{-6} mol), cycloalkene (1×10^{-4} mol) in CH_2Cl_2 (3 cm^3), reaction time 30–60 min. [b] Based on PhIO. [c] Conversion of PhIO into epoxide and allylic oxidation products. It is assumed that the formation of ketone consumes two molecules of PhIO. [d] Oxidant accountability in brackets assumes ketone formation consumes one molecule of PhIO. [e] Enol and enone identified by GC–MS, not separated by GC; combined yield 3%. [f] Trace yield (< 1%) detected by GC–MS. [g] 36:64 mixture of *cis*- and *trans*-alkenes. [h] *cis*- and *trans*-Epoxide, in the proportions 69:31. [i] Detected by GC–MS.

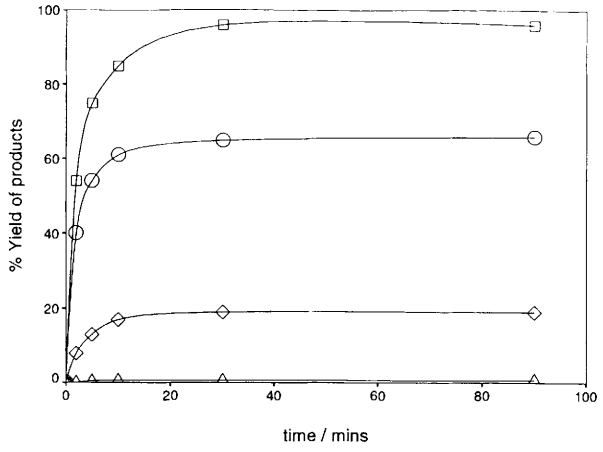


Fig. 2 Time dependence of product yields from the oxidation of cyclopentene by iodosylbenzene catalysed by $Fe^{III}TDCPP$: $Fe^{III}TDCPP$, 5×10^{-7} mol; cyclopentene, 1×10^{-3} mol; PhIO, 5×10^{-5} mol in CH_2Cl_2, 3 cm^3 at room temperature under nitrogen (□, PhI; ○, epoxycyclopentane; ◇, cyclopent-2-en-1ol; △, cyclopent-2-en-1-one)

essentially gave epoxide as the sole alkene oxidation product. Trace amounts of enols and enones (< 1%) were detected by GC–MS analysis. GC analysis of products from the cycloheptene–$Mn^{III}TDCPP$ oxidation gave a small peak (*ca.* 3% yield) which GC–MS showed to be a mixture of enol and enone.

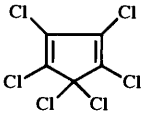
The product distributions and yields from oxidations using $Fe^{III}TDCPP$ were insensitive to the presence of dioxygen. Interestingly, however, when the reactions of cyclopentene and cyclohexene were left for 24 h there were small but significant increases in the yields of allylic oxidation products from a relatively slow background metalloporphyrin-catalysed autoxidation.[10] By comparison, the yields of oxidation products from the $Mn^{III}TDCPP$-catalysed reactions were influenced by dioxygen. This is clearly apparent from the > 100% oxidant accountability for the reactions that gave allylic oxidation products and the marked decrease in product yields from cyclohexene when dioxygen was absent.

The commercial cyclododecene substrate was a mixture of (*Z*) and (*E*) isomers; the proportions of (*Z*):(*E*) alkene were estimated by GC analysis to be 36:64. These values are comparable to the 34:66 ratio reported for the acid catalysed equilibration of cyclododecene at 100 °C.[11] Oxidation of this isomeric mixture gave two epoxides; the major one, based on the known stereopreference of iron(III) porphyrin systems, is assigned to *cis*-epoxycyclododecane. Assuming a substrate (*Z*):(*E*) ratio of 36:64, the rate of epoxidation of the (*Z*) relative to the (*E*) isomer is 3.8:1 and 4:1 for the $Fe^{III}TDCPP$ and $Mn^{III}TDCPP$ systems, respectively. These ratios compare favourably with the values, 1.5–8.9, reported by Groves and Nemo[6a] for this competitive oxidation with a selection of other synthetic iron(III) porphyrins.

Discussion

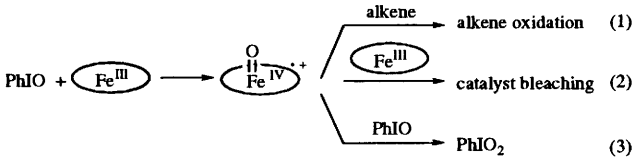
In alkene oxidation by iodosylbenzene–metalloporphyrin systems, the active oxidant is considered to be an oxometal species two oxidation levels above the starting porphyrin.[1] For iron, this intermediate is an oxoiron(IV) porphyrin π radical cation ($OFe^{IV}P^{\cdot+}$), whereas for manganese it is an oxomangan-

Table 3 Relative reactivities of the C=C bond in cycloalkenes in a selection of reactions

Reagent	Reactivity relative to cyclohexene				Ref.
CH_3CO_3H	1.5	1.0	1.4	—	14
Br_2	1.3	1.0	—	—	15
ISCN	2.1	1.0	1.9	1.1	16
CBr_2	1.25	1.0	—	—	17
PhIO/Fe^{III}T4MPyP	1.1	1.0	—	1.0	18
C_6F_5IO/Fe^{III}TDCPP	—	1.0	—	1.4	19
N_2H_2	15.5	1.0	12.1	17.0	20
$(Am^i)_2BH$[a]	108	1.0	554	2046	21
	22	1.0	29	77	22
$^{\cdot}CCl_3$	3.3	1.0	—	—	23
CF_3CO_2H	1.2	1.0	3.7	8.1	24

[a] Am = amyl.

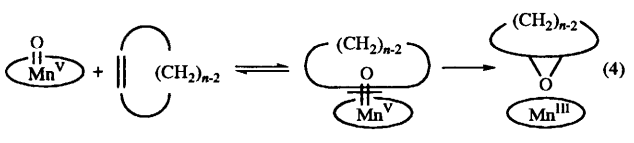
ese(v) porphyrin (OMn^VP).[1] Further reactions of these species involve alkene oxidation, together with catalyst destruction and the oxidation of PhIO to $PhIO_2$ [overall the last reaction is equivalent to the iron(III) porphyrin-catalysed disproportionation of iodosylbenzene] [reactions (1)–(3)].[12] Consequently



these oxidations are in effect competitive reactions since the active oxidant is partitioned between substrate, metalloporphyrin and iodosylbenzene. If the same initial concentrations of reactant, catalyst and oxidant are maintained for all the oxidations, the yields of alkene oxidation products give an approximate measure of the relative reactivities of the alkenes.[4b]

For each catalyst system, the conversion of iodosylbenzene to alkene oxidation products was very high, showing that alkene oxidation [reaction (1)] dominates and the alkenes effectively trap most of the active oxidant. Furthermore, the major product in each reaction was the epoxide. This is to be expected since the cyclic alkenes were present in large excess and (*Z*)-dialkylalkenes are known to be good substrates for these metalloporphyrin-catalysed epoxidations.[4a,b,6a]

Monitoring the time dependence of the formation of epoxide for each substrate did not reveal any large effects of ring size on the rates or final yields of epoxidation. This can be accounted for if it is assumed that epoxidations by $OFe^{IV}P^{\cdot+}$ and OMn^VP occur by a concerted oxygen transfer from an initially formed charge transfer complex between oxometalloporphyrin and alkene [*e.g.* reaction (4)].[2,13]

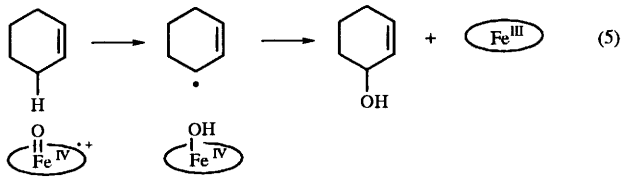


Previous studies on additions to cyclic alkenes have revealed that the rates of reactions that proceed *via* a three-membered cyclic transition state show very small ring size effects (Table 3).

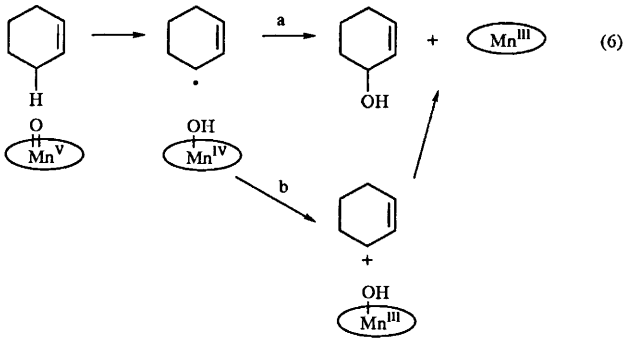
The results from a recent kinetic study on alkene epoxidation by PhIO and iron(III) tetra(4-*N*-methylpyridyl)porphyrin in methanol are in agreement with this conclusion.[18] This investigation, which is closely related to the present study, showed that the relative reactivities of cyclopentene, cyclohexene and (*Z*)-cyclooctene were almost identical. Awasthy and Rocek[25] have argued that changing the double bond into a three-membered cyclic transition state is unlikely to produce large changes in strain and consequently the rates of such processes will not show a large dependence on ring size. In contrast, additions to double bonds involving larger cyclic transition states or non-concerted processes can lead to a change in strain and the rates of these reactions generally show more significant ring size effects (Table 3).

By comparison with epoxidation, the effect of ring size on allylic oxidation is large. Thus for cyclopentene, cyclohexene and the mixture of (*Z*)- and (*E*)-cyclododecene, allylic oxidation is a significant oxidation pathway, whereas for cycloheptene, (*Z*)-cyclooctene and (*Z*)-cyclodecene the oxidation proceeds almost entirely by epoxidation.

The generally accepted mechanism for allylic oxidation by $OFe^{IV}P^{\cdot+}$ and OMn^VP is a two step process involving an initial H-atom abstraction followed by hydroxyl transfer from metal to carbon (oxygen rebound mechanism) [reactions (5) and (6)].[5b,6a,12a,26] With iron porphyrins the second step is very

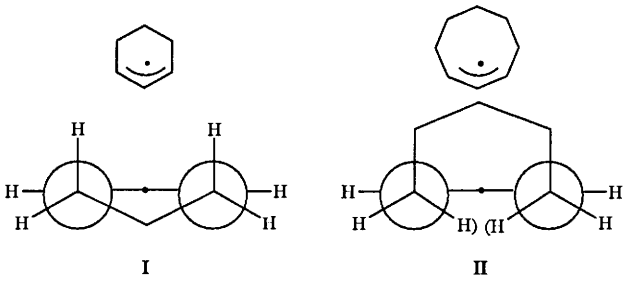


rapid.[4c] Radical probe and radical clock investigations of non-allylic aliphatic hydroxylation by microsomal cytochrome P450 provide confirmation for the great rapidity of the oxygen rebound step of iron porphyrins.[27] (Note, however, that a very recent study using a hypersensitive radical probe calls into question the involvement of a carbon radical in aliphatic hydroxylation by cytochrome P450.[28]) In contrast, the oxygen rebound for the analogous manganese systems is comparatively slow.[26b] Indeed for the latter system an alternative oxidation pathway involving electron transfer, to give an allylic cation, and ion-pair collapse may also occur.[26b] As a consequence, with

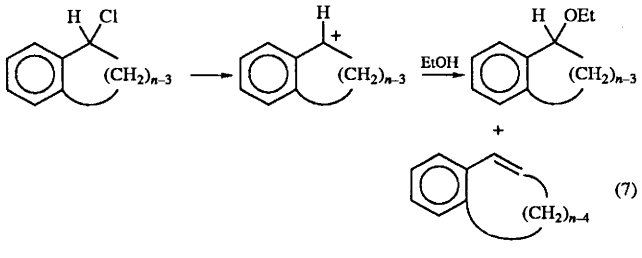


the iron system the allyl radical is very effectively oxidised by the oxoiron(IV) porphyrin within a solvent cage, whereas with the manganese system it can escape to be trapped and further oxidised by PhIO[29] or dioxygen. This difference in the two systems accounts for the dioxygen dependence of the product distribution and the greater than 100% oxidant accountability in the Mn^{III}TDCPP-catalysed oxidations which show significant allylic oxidation (cyclopentene, cyclohexene and the mixture of (*Z*)- and (*E*)-cyclododecene).

We attribute the differences in the extent of allylic oxidation of the cyclic alkenes to the influence of ring size on the stability of the allyl radical and its preceding transition state. For maximum resonance stabilisation the preferred conformation of the cyclic allyl radicals has five coplanar carbons. In cyclopentene and cyclohexene H-atom abstraction generates an allyl radical in, or close to, its preferred conformation **I**. As a



consequence, the proportion of allylic oxidation relative to epoxidation is higher with these ring systems than for the medium sized rings or acyclic (*Z*)-alkenes. Furthermore, we suggest that with medium sized rings the increased coplanarity in passing from the reactant to the transition state leads to an increase in non-bonded interactions and strain (**I** strain)[9a] in the transition state for H-atom abstraction leading to **II** with the consequence that epoxidation occurs at the expense of allylic oxidation. A confirmation for the explanation above comes from the similar trend in reactivity that has been reported for the rates of S_N1 solvolyses of 1,2-benzo-3-chlorocycloalkanes [reaction (7)],[30] where the formation of a benzyl cation leads



to a comparable increase in coplanarity from four atoms in the substrate to five in the intermediate. The rates of five-, seven- and eight-membered rings relative to the benzocyclohexane are 3.7 (benzocyclopentane):1.0 (benzocyclohexane):3 × 10^{-2} (benzocycloheptane):4 × 10^{-3} (benzocyclooctane). The five-membered ring, which most readily accommodates the resonance stabilised benzyl cation, reacts fastest, whereas the seven- and eight-membered rings, where coplanarity of five carbons is not favoured, react dramatically slower.

The origin of the significant yield of allylic products from the oxidation of cyclododecene is uncertain and is complicated by the reactant being a mixture of (*Z*) and (*E*) isomers. These products may, in part, arise from the (*E*)-alkene since (*E*)-dialkylalkenes are more prone to allylic oxidation than their (*Z*) isomers.[4b] However, the reactions are competitive oxidations of (*Z*) and (*E*) isomers and the yields of allylic products are greater than would be expected from this route alone. An alternative explanation would require that the preferred conformation of the C_{12} ring favours allylic oxidation.

Experimental

Materials

The cycloalkenes were commercially available and purified by passage through a short activated alumina column. The purities were checked by GC analysis. The iodosylbenzene and iron(III) and manganese(III) tetra(2,6-dichlorophenyl)porphyrins were prepared as described previously.[7b,18]

Instrumentation

GC analyses were carried out on Pye Unicam 204 and AMS 94 gas chromatographs equipped with flame ionisation detectors. Product separation was achieved using either a packed glass column (10%, w/w Carbowax 20 M on Celite, 100–120 mesh) or a capillary column (SGE, QC3/BP-1, 25 m × 0.32 mm id). The results were recorded and processed on a Trivector Trilab 2000 data station. ^{1}H NMR spectra were recorded on a Bruker MSL 300 spectrometer (300 MHz).

Oxidation procedure

The cycloalkene (1 × 10^{-3} mol) was stirred with the metalloporphyrin catalyst (5 × 10^{-7} mol) in dichloromethane (3 cm^3) and the reaction initiated by the addition of oxidant (5 × 10^{-5} mol). The reactions were monitored at regular intervals for 90 min by removing samples with a syringe for GC analysis. A final analysis was recorded after 24 h. All reactions were carried out in duplicate.

Anaerobic reactions were performed in a flask sealed with a Subaseal or viton septum, by bubbling nitrogen or argon through a solution of the reactants for 15 min. The reaction was initiated either as above with PhIO or, with PhIO present in the initial solution, by addition of a solution of the catalyst.

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