Reactions in Thermotropic Liquid Crystals: Epoxidations catalysed by Oriented Metalloporphyrins

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Manganese porphyrins oriented both parallel and perpendicular to the director of a nematic liquid crystal have been used as catalysts for the epoxidation of aligned alkenes.

The study of reactions in organized media such as lyotropic or thermotropic liquid crystals are of great current research interest due to their importance in understanding the organization dependence of chemical reactions and biological membrane behaviour.[1] In this context, an understanding of the chemistry of porphyrins and metalloporphyrins is of special relevance due to the part these compounds play in many different processes including photosynthesis,[2] dioxygen and electron transport[3] and catalytic oxygenation.[4] In the past, we have been able to achieve control of porphyrin orientation in both lyotropic[5] and thermotropic[6] liquid crystal host phases by attaching molecularly compatible (to the host) appendages to the porphyrin ring. In this paper we present our results on the effect of the molecular orientation of manganese porphyrins in nematic thermotropic liquid crystals on the catalytic epoxidation of alkenes. We have found that for rod-like alkene substrates the alignment of the substrate and the position of the double bond relative to that of the manganese porphyrin catalytic centre controls the epoxidation yield. On the other hand for a ball-like substrate, no orientational effect were observed.

In a nematic thermotropic liquid crystal host phase† we have shown by EPR spectroscopy that a tetraphenylporphyrin (TPP) is aligned so that the porphyrin ring is parallel to the director, **n**, whereas for a porphyrin with mesogenic 'arms' attached orthogonally to the porphyrin ring, *i.e. meso*-tetra{α,α,α,α-*o*-[4-(4-n-butoxyphenyl)phenylacetamido)} porphyrin (MesogenP) the porphyrin ring is oriented perpendicular to the director, Fig. 1.[6] Manganese(III) porphyrins were synthesized from the freebase compounds using a common metallation procedure‡ and were shown to be authentic Mn^{III} porphyrins by their visible spectrum (λ_{max} 372, 400, 476, 576, 618 nm). Epoxidation reactions were run at 20 ± 0.5 °C both in a liquid crystalline 4-cyano-4′-hexylbiphenyl

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† The host phase was 4-cyano-4′-hexylbiphenyl (BDH K18) with $C \rightarrow N$ 14.5 °C and $N \rightarrow I$ 29 °C.

‡ The free base H_2MesogenP porphyrin was dissolved in tetrahydrofuran and a 100-fold excess of manganesese(II) acetate was added and the mixture heated under reflux for 24 h. Isolation of the MnMesogenP was by the typical workup.

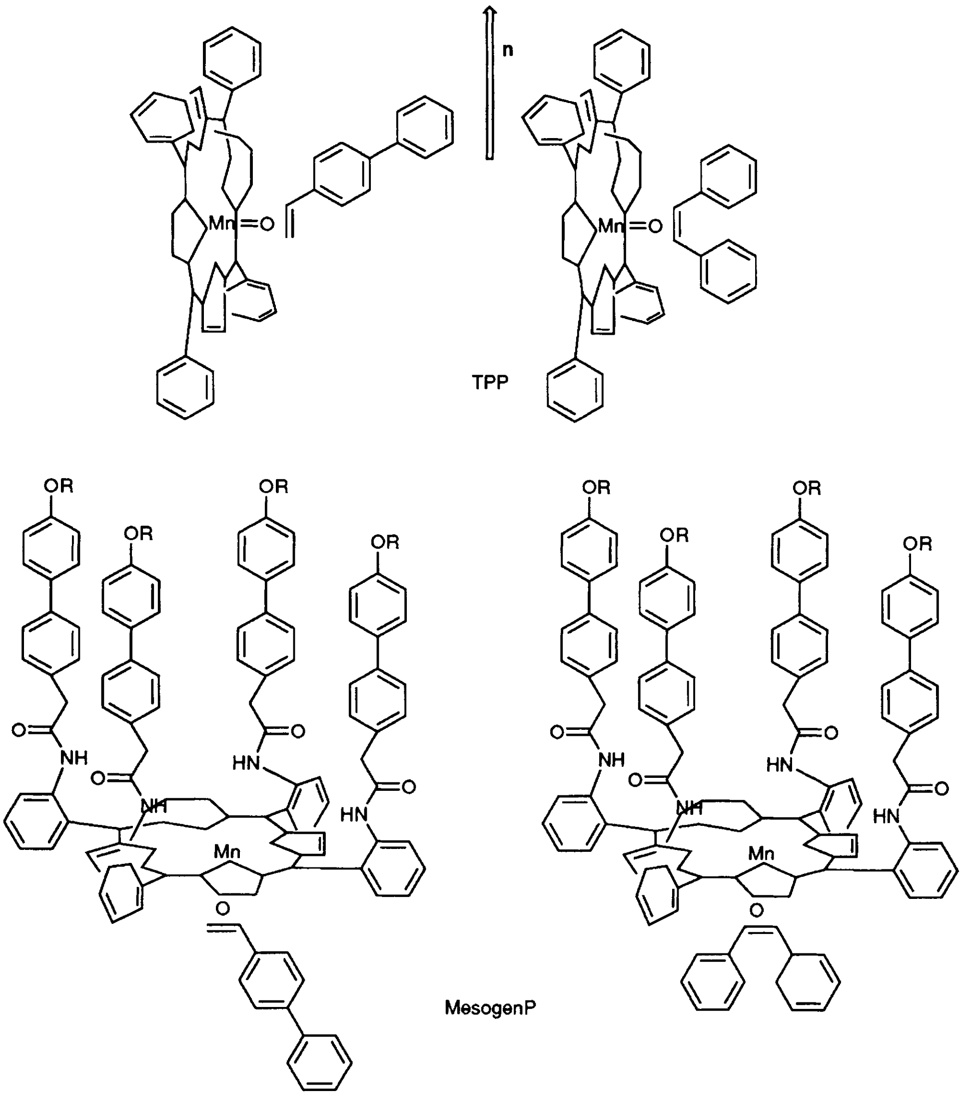

Fig. 1 Idealized representation of porphyrin and substrate orientation within a nematic liquid crystalline phase

solvent and the isotropic dichloromethane (DCM) solvent using iodosobenzene as the primary oxidant. Quanitization of the results was by GLC.

The results of the epoxidation of two rod-like substrates, (*Z*)-stilbene and 4-vinylbiphenyl, and a ball-like substrate, (*Z*)-cycloctene, reveal all the essential features of the substrate, host, and porphyrin spacial interactions in both single substrate reactions and competitive reactions, (Table 1). First, examination of the results in reactions that have no spacial constraints *i.e.* DCM solvent and MnTPP catalyst shows the following relative substrate reactivity 4-vinylbiphenyl > (*Z*)-stilbene > (*Z*)-cycloctene (runs 4, 8, 12, 16). Similar reactions in DCM with MnMesogenP as catalyst show that the latter is a slightly better catalyst than MnTPP for 4-vinylbiphenyl and (*Z*)-cycloctene as substrates (run 11 *vs.* 12 and 7 *vs.* 8), however, for (*Z*)-stilbene a significant 50% reduction (run 3 *vs.* 4 also 15 *vs.* 16) in the epoxidation yield was observed. We explain the lower yield for (*Z*)-stilbene as being due to steric hindrance preventing approach of the substrate to the substituted face of MesogenP, statistically reducing the reaction probability by 50%. The (*Z*)-stilbene oxide: (*E*)-stilbene oxide ratios of 3–4 : 1 are indicative of a catalytic system with both $Mn^{IV}=O$ and $Mn^{V}=O$ as active oxygen donors,[7] since the former has been found to yield the (*Z*)-oxide, as the major product and the latter yields principally the (*E*)-oxide.

Turning our attention to the reactions performed in the liquid crystal solvent, one may observe that for (*Z*)-stilbene where the preferred alignment of the substrate is perpendicular to that of the porphyrin ring (MnMesogenP) there is no reaction (runs 1 and 13). The idealized relative catalyst–substrate orientations as shown in Fig. 1 are based on the assumption that epoxidation takes place upon interaction of an electrophilic metal–oxo species[8] and the nucleophilic p orbital (HOMO) of the alkene. When the orientation of (*Z*)-stilbene is parallel to that of the porphyrin as in MnTPP as catalyst there is epoxidation although in general reactions are less efficient than those in the isotropic solvent (run 2 and 14). With 4-vinylbiphenyl as substrate the preferred ideal alignment of the substrate relative to the MnTPP catalyst forces the biphenyl moiety to 60° relative to the director, leading to a lower yield (run 6 and 14). However, in the case of MnMesogenP as catalyst the ideal orientation of the biphenyl group is only 30° relative to the director and yields are significantly higher (run 5 and 13). Competitive experiments in a liquid crystal phase most clearly show the orientational effects on the substrate–catalyst interaction leading to high regioselectivities.

(*Z*)-Cycloctene as substrate shows as expected that there are no orientational effects for ball-like substrates in liquid crystal hosts and results are similar to those found for a typical isotropic solvent. It is important to note that although the

Table 1 Epoxidations in nematic and isotropic phases[a]

	Single Substrate				
Run	Solvent	Substrate	Catalyst	Turnovers[b]	Iodosobenzene conversion[c]
1	LC-K18	(*Z*)-Stilbene	MnMesogenP	0.0	40
2	LC-K18	(*Z*)-Stilbene	MnTPP	14.8[d]	43
3	DCM	(*Z*)-Stilbene	MnMesogenP	11.7[d]	62
4	DCM	(*Z*)-Stilbene	MnTPP	24.8[d]	68
5	LC-K18	4-Vinylbiphenyl	MnMesogenP	44.4	57
6	LC-K18	4-Vinylbiphenyl	MnTPP	19.1	62
7	DCM	4-Vinylbiphenyl	MnMesogenP	51.5	81
8	DCM	4-Vinylbiphenyl	MnTPP	45.0	72
9	LC-K18	(*Z*)-Cycloctene	MnMesogenP	6.3	49
10	LC-K18	(*Z*)-Cycloctene	MnTPP	3.1	50
11	DCM	(*Z*)-Cycloctene	MnMesogenP	9.7	57
12	DCM	(*Z*)-Cycloctene	MnTPP	3.9	57
Competitive experiments					
13	LC-K18	(*Z*)-Stilbene and 4-vinylbiphenyl	MnMesogenP	0 66.1	85
14	LC-K18	(*Z*)-Stilbene and 4-vinylbiphenyl	MnTPP	21.2 3.6	73
15	DCM	(*Z*)-Stilbene and 4-vinylbiphenyl	MnMesogenP	13.1 40.0	80
16	DCM	(*Z*)-Stilbene and 4-vinylbiphenyl	MnTPP	25.3 41.1	82

[a] Reactions were performed by mixing manganese porphyrin (0.156 mmol), substrate (24 mmol) and iodosobenzene in solvent (0.2 ml) [LC-K18= 4-cyano-4′-hexylbiphenyl) at 20 °C for 4 h. [b] Turnovers represent mol epoxide formed per mol catalyst. [c] Mol iodobenzene formed per mol catalyst (computed by GLC from the ratio of iodobenzene formed to the total amount of alkene and epoxide at the end of the reaction). [d] The ratio of (*Z*)-stilbene oxide : (*E*)-stilbene oxide varied between 3.2 and 4.1.

analysis of the results has been carried out using an idealized representation of the orientation of the catalyst and substrate, a real picture must take into account orientational fluctuations relative to the director (even if these fluctuations average out) and perturbations in the liquid crystal phase especially with MesogenP where the porphyrin ring is perpendicular to the director. Despite these limitations, however, we feel that the evidence indicates strong orientational effects.

Received, 5th March 1993; Com. 3/01315D

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