Pergamon

Tetrahedron Letters, Vol. 38, No. 41, pp. 7283-7286, 1997

PII: S0040-4039(97)01692-4

0040-4039/97 $17.00 + 0.00

Epoxidation and Hydroxylation Reactions Catalysed by β-Tetrahalogeno and β-Octahalogeno Manganese Porphyrins.

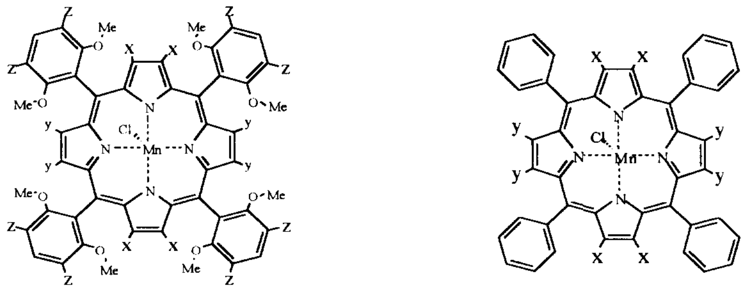
Enrico Baciocchi,* Tristano Boschi,[a] Luigi Cassioli, Carlo Galli, Andrea Lapi, Pietro Tagliatesta[a]

Dipartimento di Chimica, Università "La Sapienza", P.le A. Moro, 00185 Roma, Italy.
a) Dipartimento di Scienze e Tecnologie Chimiche, Università di Tor Vergata,
Via della ricerca scientifica, 00133 Roma, Italy.

Abstract: *β-Tetrahalogenated manganese(III) porphyrins are more efficient catalysts than the β-octahalogenated ones in oxidations promoted by* H_2O_2.

Synthetic metalloporphyrins, in particular iron and manganese tetraarylporphyrins, are efficient catalysts in the hydroxylation of alkanes and epoxidation of alkenes promoted by a variety of oxidants like iodosylarenes, hypochlorites, alkyl hydroperoxides, hydrogen peroxide.[1]

Recently, the recognition that the introduction of Cl or Br atoms into metalloporphyrins significantly increases their catalytic activity has promoted the synthesis of metalloporphyrins where all the ß-pyrrolic positions are halogenated[2] with the reasonable presumption that these should be the best catalysts. However we now report that, with H_2O_2 as the oxygen donor, the manganese(III) tetra-β-halogeno porphyrins, **1-4** and **2-4**, are more efficient catalysts than the corresponding octahalogenated ones, **1-8** and **2-8**, both in the hydroxylation of adamantane and in the



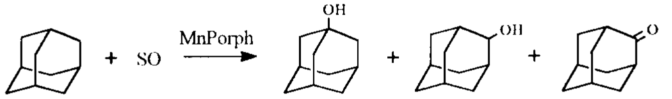
1-0: x=y=z=H
1-4: x=z=Cl, y=H
1-8: x=y=z=Cl

2-0: x=y=H
2-4: x=Br, y=H
2-8: x=y=Br

Figure 1. Structure of the halogenated Mn(III)porphyrin complexes used in this study.

epoxidation of cyclooctene. In contrast, results in line with expectations were obtained when iodosylbenzene is the oxygen donor.

The oxidation of adamantane leads to 1-adamantanol, 2-adamantanol, adamantanone (eq. 1) and a very minor amounts of dioxygenated products. The results are reported in Table 1.



(1)

It clearly appears that when H_2O_2 is the oxidant, the tetrahalogenated manganese porphyrins **1-4** and **2-4** are more efficient catalysts than the manganese-octahalogenated porphyrins **1-8** and **2-8**. Both **1-4** and **2-4** also outdo the corresponding β-unsubstituted manganese porphyrins **1-0** and **2-0** in catalytic activity (compare entry 2 with 1 and 3, and entry 5 with 4 and 6). It would seem as if the progressive introduction of β-halogens would first increase and then decrease the catalytic efficiency of the manganese porphyrins. A different situation holds in the reactions with PhIO (entries 7-9), where a gradual increase in the yield of the oxidised products on going from **1-0** to **1-4** and **1-8** is observed.

Table 1. Product yields and reaction conditions for the oxidation of adamantane with H_2O_2 or PhIO catalysed by Mn(III)tetraarylporphyrins bearing a different number of β-halogen groups.

Oxygen donor (SO)	Entry	Catalyst	Sub/Ox/Porph	Time	Tot. yield (%)[c]
H_2O_2[a]	1	**1-0**	40/200/1	2 h	18
	2	**1-4**			72
	3	**1-8**			27
	4	**2-0**			7.0
	5	**2-4**			39
	6	**2-8**			27
PhIO[b]	7	**1-0**	800/20/1	1 h	30
	8	**1-4**			65
	9	**1-8**			76

a) Oxidation reactions with H_2O_2 are carried out in the presence of imidazole (Imidazole/Porphyrin=25:1) in C_6H_6/CH_3CN 1:1; total yields (determined by GLC) are based on the substrate.

b) Oxidation reactions with PhIO are carried out in C_6H_6; total yields (determined by GLC) are based on the oxidant.

c) Errors based on duplicated experiments are 5%

Similar results (Table 2) are obtained in the epoxidation of cyclooctene. Thus, if H_2O_2 is the oxidant, a higher yield of cyclooctene epoxide is obtained with **1-4** than with **1-8**. A similar catalytic activity is found for **1-4** and **1-0**. If the epoxidation is carried out with PhIO, the epoxide yields seem to be independent of the number of β-halogen atoms. This is probably due to the high efficiency of the epoxidation reaction, under these conditions, which apparently levels out the catalytic efficiency of the three manganese porphyrins.

These interesting and unexpected results show that, when H_2O_2 is the oxygen donor, there is no simple relationship between catalytic activity and number of halogen atoms in the β-positions, the activity of the β-tetrahalogenated manganese porphyrins being higher than that of the corresponding β-octahalogenated ones.

Table 2. Product yields and reaction conditions for the oxidation of cyclooctene with H_2O_2 or PhIO catalysed by Mn(III)tetraarylporphyrins bearing a different number of β-halogen groups.

Oxygen donor (SO)	Entry	Catalyst	Sub/Ox/Porph	Time	Yield (%)$^{(c)}$
$H_2O_2^{(a)}$	10	**1-0**	40/80/1	1.5 h	61
	11	**1-4**	40/80/1		64
	12	**1-8**	40/80/1		46
PhIO$^{(b)}$	13	**1-0**	400/20/1	0.5 h	87
	14	**1-4**	400/20/1		82
	15	**1-8**	400/20/1		84

a) Oxidation reactions with H_2O_2 are carried out in the presence of imidazole (Imidazole/Porphyrin = 25:1) in CH_2Cl_2/CH_3CN 1:1; total yields (determined by GLC) are based on the substrate.

b) Oxidation reactions with PhIO are carried out in CH_2Cl_2; total yields (determined by GLC) are based on the oxidant.

c) Errors based on reproduced experiments are 5%

As a possible explanation, it might be suggested that full substitution of the β positions of pyrrole rings by halogens makes the manganese porphyrins less robust toward H_2O_2 than when only four β halogen atoms are present. Accordingly, the presence of eight β-halogens distorts the structure of the porphyrin from planarity[3] and this might make it more susceptible to attack either by H_2O_2 itself or by other radical species derived from it[4]. In contrast to this explanation, however, we have observed that our tetra- and octahalogenated catalysts suffer from bleaching to a comparable extent (i.e. 76 and 78% bleaching for **1-4** and **1-8** respectively in the reaction with adamantane). Moreover, when **2-8** was recovered after the H_2O_2-induced epoxidation of cyclooctene and then subjected to FAB analysis, it turned out that all the eight bromine atoms were still present. Thus, we tentatively suggest that our results originate from the fact that the manganese tetrahalogenated porphyrins are more efficient than the octahalogenated ones in the preliminary formation of the metallo oxo complex by heterolytic cleavage of H_2O_2. Distortion from planarity of the octahalogenated porphyrin might play a role in this respect making more difficult the simultaneous coordination of H_2O_2 and imidazole with the metallic centre, which is known to favour the heterolytic cleavage of the O-O peroxidic bond[5]. This hypothesis might also be consistent with the fact that differences in catalytic activity between the tetra- and the octahalogenated manganese porphyrins are more marked with the more hindered tetra(2,6-dimethoxyphenyl)porphyrins than with the tetraphenyl porphyrins (Table 1). On the other hand, when PhIO is the oxidant, the formation of the metallo oxo complex is a straightforward process, which by no means presents the problems associated to the use of H_2O_2 or hydroperoxides as oxygen donors. Accordingly, no 'bell shape' trend of the yields is observed in the reactions promoted by PhIO, the catalytic efficiency of the octahalogenated porphyrins being higher or comparable to that of the tetrahalogenated ones, as expected.

Acknowledgements.

Financial support to this investigation from the Ministry of University and the Scientific and Technological Research (MURST) is gratefully acknowledged.

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(*Received in UK* 24 *July* 1997; *accepted* 15 *August* 1997)