

## Porphyrimatoiron-catalysed Reduction of Styrene with Sodium Borohydride: Proposed $\sigma$ -Alkyliron(III) Complex as an Intermediate

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5,10,15,20-Tetrakis(*para*-substituted phenyl)porphyrimatoiron(III) chloride complexes catalyse the reduction of styrene with NaBH<sub>4</sub> to ethylbenzene and 2,3-diphenylbutane and the precursor is assumed to be the  $\sigma$ -alkyl complex (Xtpp)Fe<sup>III</sup>-PhCHMe.

Several groups have reported metalloporphyrin-catalysed oxygenation reactions of alkenes in organic and aqueous solutions containing NaBH<sub>4</sub>.<sup>1-5</sup> Santa *et al.*<sup>4</sup> assumed that an Fe<sup>V</sup>-oxo porphyrin was an intermediate for the Fe(tpp)<sup>+</sup>-catalysed oxygenation of alkenes to the corresponding alcohols in benzene-ethanol in the presence of NaBH<sub>4</sub>. If the

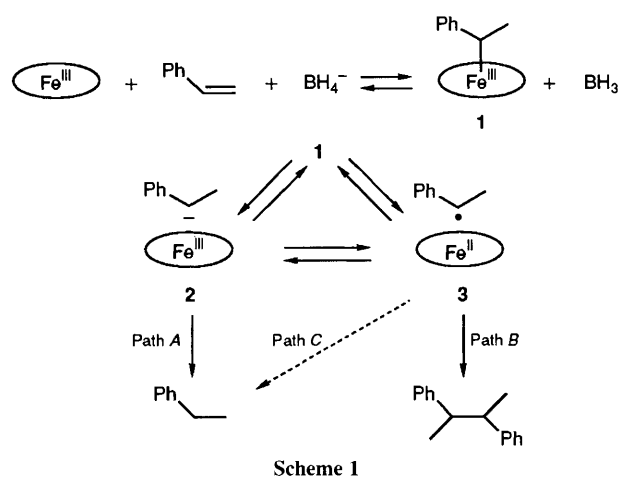
oxygenation occurs *via* an Fe<sup>V</sup>-oxo porphyrin, the primary products would be expected to be epoxides.<sup>6</sup> In spite of the relatively slow reduction of epoxides with BH<sub>4</sub><sup>-</sup>, no epoxides have been detected in the alkene-metalloporphyrin-BH<sub>4</sub><sup>-</sup> system. The mechanism involving an Fe<sup>V</sup>-oxo porphyrin, therefore, is doubtful. In this communication, we report the first example of the porphyrimatoiron-catalysed reduction of styrene with NaBH<sub>4</sub> in anaerobic organic solvents. The results imply a  $\sigma$ -alkyliron(III) porphyrin complex as an intermediate which is also assumed to be the intermediate for the oxygenation of alkenes.

† [Fe<sup>III</sup>(Xtpp)]Cl = 5,10,15,20-tetrakis(*para*-substituted phenyl)-porphyrimatoiron(III) chloride; tpp = 5,10,15,20-tetraphenylporphyrin dianion.

**Table 1** Fe<sup>III</sup>(Xtp<sub>p</sub>)-catalysed reactions of styrene with NaBH<sub>4</sub> in anaerobic organic solvents

Entry	X in [Fe <sup>III</sup> (Xtp <sub>p</sub> )(Cl)]	Solvent <sup>a</sup>	Time/h <sup>b</sup>	Yield (%)		
				EB	<i>meso</i> - DPB	(±)-DPB
1	H	EtOH	1	65	7	7
2	H	C <sub>6</sub> H <sub>6</sub> <sup>c</sup>	24	0	7	7
3	H	C <sub>6</sub> H <sub>6</sub> -EtOH	6	13	22	14
4	H	C <sub>6</sub> H <sub>6</sub> -MeCN <sup>c</sup>	24	0	12	8
5	Cl	EtOH	1	81	6	5
6	Cl	EtOH-MeCN	6	22	16	18
7	Cl	C <sub>6</sub> H <sub>6</sub> -EtOH	6	76	6	7
8	Cl	C <sub>6</sub> H <sub>6</sub> -Pr <sup>i</sup> OH <sup>c</sup>	24	4	13	10
9	CN	C <sub>6</sub> H <sub>6</sub> -EtOH	24	20	20	22
10	Me	C <sub>6</sub> H <sub>6</sub> -EtOH	24	57	9	10
11	OMe	C <sub>6</sub> H <sub>6</sub> -EtOH	6	10	9	10

<sup>a</sup> The ratio for mixed solvents is 1:1 v/v. <sup>b</sup> Time for complete consumption of styrene. <sup>c</sup> In these systems, 15-crown-5 was used to dissolve NaBH<sub>4</sub>.



The products in the [Fe<sup>III</sup>(Xtp<sub>p</sub>)]Cl-catalysed reaction of styrene with NaBH<sub>4</sub> are ethylbenzene (EB) and *meso*- and (±)-2,3-diphenylbutane (DPB).<sup>‡</sup> The results are summarized in Table 1.

The formation of EB needs protic solvents such as ethanol or propan-2-ol. The reactions in benzene (entry 2) and benzene-acetonitrile (entry 4) do not provide EB at all while DPB is formed in low yields (14–20%). In order to study the origins of the hydrogen atoms at the α- and β-positions of EB, the reactions were carried out using C<sub>2</sub>H<sub>5</sub>OD and NaBD<sub>4</sub>. The results clearly indicate that the α- and β-hydrogens of EB originate from the hydroxy proton of ethanol and the hydride of BH<sub>4</sub><sup>-</sup>, respectively.

DPB is formed in both protic and aprotic solvents. It was found from the deuterium incorporation experiments that a hydrogen of the methyl group at the 2-position as well as that at the 3-position of DPB is donated from the BH<sub>4</sub><sup>-</sup> anion.

<sup>‡</sup> In a typical reaction, styrene (1.5 mmol) was added to a mixture of [Fe<sup>III</sup>(Xtp<sub>p</sub>)]Cl (0.15 mmol) and NaBH<sub>4</sub> (3.0 mmol) in 8 ml of nitrogen-saturated benzene-ethanol (1:1). The reaction was carried out by stirring the mixture at ambient temperature under nitrogen. Deaeration, however, was not strictly performed in these reactions. The reaction products were isolated by silica gel column chromatography and analysed by means <sup>1</sup>H NMR spectroscopy and GC-mass spectrometry.

These results can be explained by the mechanism shown in Scheme 1. The key in this mechanism is the formation of the σ-alkyliron(III) complex, **1**, formed by ligation of 1-phenylethanide to Fe<sup>III</sup>(Xtp<sub>p</sub>). In polar solvents, **2** having a polar structure seems to be stabilized by extensive solvation. When **2** is surrounded by protic polar solvent molecules, the proton transfer from solvent to 1-phenylethanide may easily occur to afford EB (Path A). The equilibria between **1** and **3** and between **2** and **3** need to be considered. The solvent-separated 1-phenylethyl radicals may couple with each other to give *meso*- and (±)-DPB (Path B).<sup>§</sup> A similar coupling reaction has been observed in the reaction of the σ-benzyl complex of Fe<sup>III</sup>(tpp) which is prepared by the reaction of Fe<sup>III</sup>(Htp<sub>p</sub>) with benzylmagnesium bromide.<sup>7</sup> Path C may be excluded from the results of the deuterium incorporation. The low yield of EB in the reaction in benzene-propan-2-ol (entry 8) also supports the absence of Path C. As shown in Table 1, in some cases, most of the styrene is consumed to give unknown product(s). Probably radical-chain reactions of styrene occur in these systems.

The mechanism shown in Scheme 1 provides a reasonable explanation of the porphyrinatoiron-catalysed oxygenation of alkenes in the presence of BH<sub>4</sub><sup>-</sup>. It has been verified that σ-alkyliron(III) porphyrin complexes react readily with oxygen to give the corresponding ketones.<sup>7</sup> Okamoto and Oka<sup>3</sup> proposed a similar mechanism involving the σ-alkyl complex of Co<sup>II</sup>(tpp) for the Co<sup>II</sup>(tpp)-catalysed oxygenation of styrene in 1,2-dimethoxyethane-propan-2-ol (1:1) containing BH<sub>4</sub><sup>-</sup>. The present results strongly support their mechanism.

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## References

- 1 I. Tabushi and N. Koga, *J. Am. Chem. Soc.*, 1979, **101**, 6456.
- 2 M. Perrée-Fauvet and A. Gaudemer, *J. Chem. Soc., Chem. Commun.*, 1981, 874.
- 3 T. Okamoto and S. Oka, *J. Org. Chem.*, 1984, **49**, 1589.
- 4 T. Santa, T. Mori and M. Hirobe, *Chem. Pharm. Bull.*, 1985, **33**, 2175.
- 5 K. Kano, H. Takagi, M. Takeuchi, S. Hashimoto and Z. Yoshida, *Chem. Lett.*, 1991, 519.
- 6 G.-X. He, H.-Y. Mei and T. C. Bruice, *J. Am. Chem. Soc.*, 1991, **113**, 5644 and references cited therein.
- 7 R. D. Arasasingham, A. L. Balch, C. R. Cornman and L. Lotos-Grazynski, *J. Am. Chem. Soc.*, 1989, **111**, 4357.

<sup>§</sup> Fe<sup>II</sup>(Xtp<sub>p</sub>), which is inactive for the reduction of styrene, may be oxidized to Fe<sup>III</sup>(Xtp<sub>p</sub>) by oxygen remaining in the reaction vessel.