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Novel Synthetic Method of Phenol from Benzene Catalysed by Perfluorinated Hemin

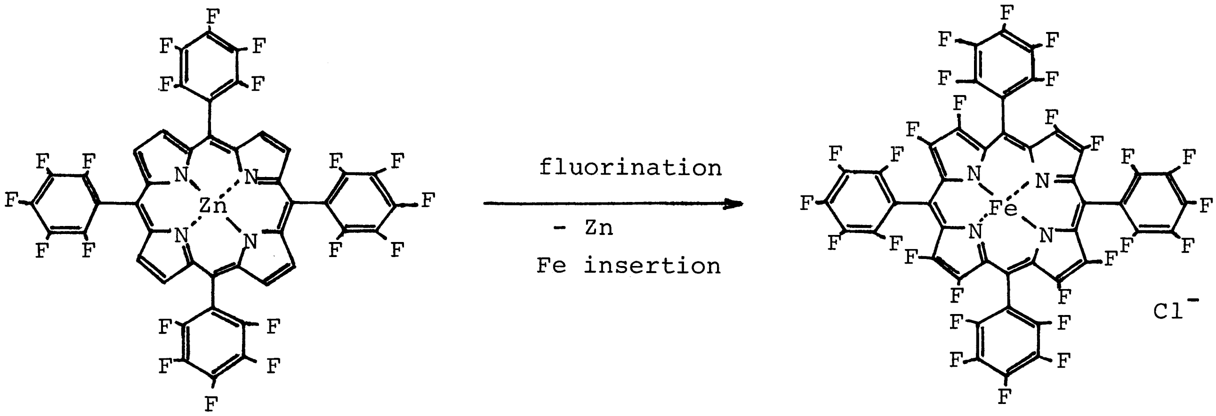
Shinji TSUCHIYA* and Manabu SENŌ
Institute of Industrial Science, The University of Tokyo,
7-22-1, Roppongi, Minato-Ku, Tokyo 106

New perfluorinated hemin carrys out hydroxylation of benzene by hydrogen peroxide at room temperature and an atmospheric pressure. The turnover for phenol produced for 2 hours is 55. This hemin also catalyses the epoxidation of cyclooctene by hydrogen peroxide.

The quantity of phenol produced industrially ranks near the top of the list of synthetic aromatic compounds. Several synthetic methods are known, but their starting materials are sodium benzene sulfonate, chlorobenzene, and cumene, and the reaction conditions of some reactions are severe.1) On the other hand, the synthetic hydroxylation reactions that are catalysed by metalloporphyrins attracted the interest of investigator, and many new porphyrins were synthesized to do this.2) However, most of metalloporphyrins were destroyed by strong oxidizing reagents such as hypochlorite, hydrogen peroxide, m-chloroperoxybenzoic acid, and iodosylbenzene, when the substrate was not added to the reaction solution. In our trials to make robust porphyrins, we found that the electronegative group on the pyrrole ring of the porphyrin makes important role to resist the porphyrin skelton to oxidative degradation.3) It is also reported that tetraphenylhemin bearing the phenyl group that is both electronegative and bulky has the property as robust catalysis.4) Thus, we made perfluorinated tetraphenylporphyrin and its metal complex. This strategy has been successful, and new porphyrin metal complexes are resistant to attack by the strong oxidizing reagents without substrates. Now, we wish to report that a new perfluorinated tetraphenylporphyrin iron complex (2) catalyses the hydroxylation of benzene to form phenol by hydrogen peroxide at room temperature and an atmospheric pressure. The spectroscopic data and structure of new perfluorinated hemin 2 are shown in below.

Table 1. The Soret absorptions of fluorinated porphyrin and related metal complexes in chloroform

Perfluorinated porphyrin	1	430 nm
Perfluorinated porphyrin iron(III)•Cl^-	2	421 nm
Tetrakis(pentafluorophenyl)porphyrin Zn complex	3	417 nm
Perfluorinated porphyrin Zn complex	4	441 nm



3 2

The preparation and assignment of this porphyrin were described as follows. 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin Zn complex (3) was prepared by condensation of pyrrole with pentafluorobenzaldehyde and Zn(OAc)$_2$ in refluxing collidine.5) The porphyrin Zn complex 3 was isolated by evaporation of collidine and purified by alumina column chromatography. This method was used to synthesize tetraphenylporphyrin having bulky substituents, but we can get the high yield by this method. The fluorination of pyrrole protons of Zn complex 3 was performed by cobalt fluoride in methylene chloride and N-containing aromatic solvent, or silver fluoride in methylene chloride. The Zn complex 3 was dissolved in above solvent and metal fluoride was added to this solution and refluxed under argon. After treatment of water and evaporation of solvent, the new porphyrin Zn complex 4 was purified by silica-gel chromatography. The fluorination of pyrrole protons of tetrakis(2,6-dichlorophenyl)porphyrin Zn complex was already performed by us,6) but this method was improved.7) The 270 MHz NMR spectrum (JEOL GX270) of this product 4 did not show any proton peaks. The mass spectrum of this porphyrin 1 showed the parent peak(1118) and the elemental analyses of carbon and nitrogen atoms were consistent with the calculated values. Visible spectrum of 4 showed a Soret absorption at 441 nm. This is 24 nm red shifted from the starting porphyrin Zn complex 3 (417 nm). After removal of Zn of complex 4, the Fe insertion was performed. The removal of Zn and insertion of Fe were performed by our method,3) including the bromination method of pyrrole protons of porphyrin skelton.

In a typical hydroxylation experiment, hemin 2 (1 x 10^{-4} M) in methylene chloride (0.1 cm^3) and benzene (3 cm^3) were stirred with 35% hydrogen peroxide (0.1 cm^3) under air for 2 hours at 25 $^{\circ}$C. (1 M = 1 mol dm^{-3}) After separation of organic layer and reduction of solvent by rotary evaporator, quantitative analyses and identifications of the products were performed by GC. 55 Equiv. of phenol, based on the amount of hemin catalysis, was produced over 2 hours (turnover = 55). The analysis of GC also shows the existence of 1,4-benzoquinone, which comes from the oxidation of phenol produced. The part of phenol produced by the hydroxylation of benzene was oxidized by hydrogen peroxide again. On the other hand, when m-chloroperoxybenzoic acid (mCPBA) was used as oxidant, major product was 1,4-benzoquinone. The reasons of these results are not yet certain. Though the mixture of methylene chloride and methanol was used as the solvent to form homogeneous system, similar results were obtained. In addition, in order to confirm the oxidation of phenol, the phenol was used as the substrate. The hemin 2 and phenol were dissolved in the mixture of methylene chloride and methanol. The hydrogen peroxide was added to this solution slowly. These reaction products were analysed by GC directly. 1,4-Benzoquinone was only product.

The peak height of visible spectrum of perfluorinated hemin 2 after hydroxylation reaction for 2 hours did not change. This indicates the remarkable stability of this perfluorinated hemin 2 toward destruction during catalysed hydroxylation of benzene.

Generally, the porphyrin iron complexes and manganese complexes catalyse the epoxidation of alkene by oxidizing agents.8) However, as far as hydrogen peroxide is concerned, a few paper on epoxidizing system using it as oxidant is reported.10) This hemin 2 also catalysed the epoxidation of cyclooctene by 35% hydrogen peroxide and these alkene were epoxidized with quantitative conversion with no hemin destruction. The experiments of epoxidation of cyclooctene were performed as follows. The cyclooctene (1 M) was added in the solution of hemin (1×10^{-3} M), which consisted of methylene chloride (0.2 cm^3) and methanol (0.2 cm^3). Upon slow addition of hydrogen peroxide (0.125 M) to a solution of cyclooctene and hemin, the conversion of alkene took place with formation of cyclooctene oxide (after 1 hour, 95% yield based on the amount of hydrogen peroxide). The hemin 2 was not destroyed at the end of the reaction as shown by the same height of hemin peak in visible spectrum. Thus, another hydrogen peroxide (0.125 M) was added and the epoxide was gained again. This procedure was repeated at 5 times (total amount of hydrogen peroxide = 0.625 M). The yield of epoxide was 0.58 M (93% yield, based on the amount of hydrogen peroxide). Though turnover for epoxidation in this experiment was 580, the hemin 2 was not destroyed during catalysed epoxidation and then, higher turnover will be gained by more addition of hydrogen peroxide. The data of oxidation of substrates were summarized in Table 2.

Table 2. Results of oxidation reaction of substrates catalysed by new perfluorinated hemin 2

Reactants	Products	Turnover
Cyclooctene	Cyclooctene oxide	580[a)]
Benzene	Phenol	55[b)]
Phenol	1,4-Benzoquinone	107[a)]

a) The analyses of GC were performed after 1 hour.

b) This number does not include the amount of 1,4-benzoqiunone.

This behaviour of hydroxylation of benzene and epoxidation of cyclooctene by new perfluorinated hemin 2 and hydrogen peroxide is similar to that of cytochrome

P-450. Thus, these results catalysed by hemin 2 suggest the mechanism of heterolytic cleavage of the O - O bond of hydrogen peroxide like cytochrome P-450.9) On the other hand, it is reported that simple Fe(III) porphyrin is unable to catalyse epoxidation of alkene by alkyl hydroperoxides.10,11,12)

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