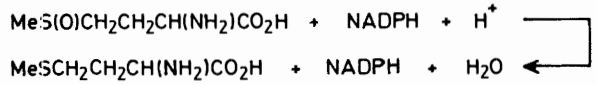
meso-Tetraphenylporphinatoiron Catalysed Reductive Cleavage of some S–O, S–N, and S–C Bonds in Sulphoxides and Sulphilimines

Toshiyuki Nagata, Ken Fujimori, Toshiaki Yoshimura, and Naomochi Furukawa
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki, 305 Japan
Shigeru Oae*
Okayama University of Science, 1-1 Ridai-cho, Okayama, 700 Japan

meso-Tetraphenylporphinatoiron chloride (TPPFe^{III}Cl) has been found to catalyse the reductive cleavage of semipolar S–O and S–N bonds in aromatic sulphoxides and sulphilimines respectively with both 1-benzyl-1,4-dihydronicotinamide (BNAH) and sodium borohydride. Sulphoxides bearing electron-withdrawing substituents are much more readily reduced than those with electron-donating groups. The rate of reduction by the TPPFe^{III}/BNAH system decreases in the following order: *N*-unsubstituted sulphilimines > *N*-tosylsulphilimines > aromatic sulphoxides. During the reaction with sulphoxides, the formation of the μ-oxo dimer of TPPFe^{III} has been observed. Under the same conditions, concurrent reductive cleavage of the S–C bond was observed with sulphoxides bearing an electron-withdrawing group at the α-position. Control experiments revealed that the reductive *S*-dealkylation of these sulphides is accompanied by the major *S*-deoxygenation reaction. Plausible mechanisms are discussed.

Both sulphoxides and sulphilimines possess reactive semipolar S–O and S–N bonds.[1] The bond energy of the sulphoxide S–O is *ca.* 87–89 kcal mol^{-1}, much less than that of the sulphones (*ca.* 112 kcal mol^{-1}),[2] and numerous reagents are known to reduce sulphoxides[3] and sulphilimines.[4] For example, iodide anion[5] and thiols[6] reduce sulphoxides *via* nucleophilic substitution on the 3-co-ordinated sulphur atom. Many sulphoxides are known to occur in living systems[7] and these sulphoxides are known to be reduced to the corresponding sulphides both *in vivo*[8,9] and *in vitro*.[10–12] For example, methionine sulphoxide is reduced enzymically to methionine with dihydronicotinamide



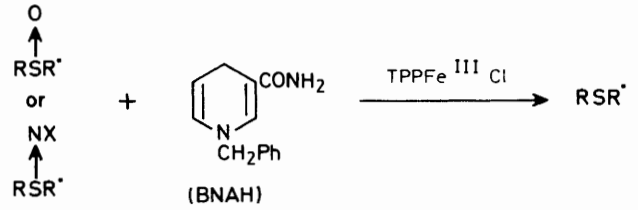
Scheme 1.

adenine dinucleotide phosphate (NADPH) (Scheme 1).[13] Biomimetic reduction of carbonyl[13,14] and thiocarbonyl[13] with 1-benzyl-1,4-dihydronicotinamide (BNAH), a model compound of NAD(P)H, is believed to proceed by a single electron-transfer mechanism. The photochemical reduction of sulphilimines with benzenethiolate anion has been found to be initiated by a photoinduced single-electron transfer from the thiolate to the sulphilimine.[15] Thus the reduction of sulphoxides and sulphilimines with BNAH was expected to proceed by a single-electron transfer mechanism. As reported in a preliminary communication, although BNAH has been found to be completely inert to sulphoxides in the absence of catalyst, it reduces them smoothly in the presence of a catalytic amount of metalloporphyrin.[16]

Since *meso*-tetraphenylporphinatoiron(III) chloride (TPPFe^{III}Cl) has been found to be the most potent catalyst of the few metalloporphyrins rested,[16] we have extended further the investigation of the TPPFe^{III} catalysed reduction of sulphoxides and sulphilimines (Scheme 2).

Results and Discussion

Reductive Cleavage of Semipolar S–O *and* S–N *Bonds.*—Reactions of BNAH with a variety of sulphoxides and



Scheme 2.

sulphilimines have been carried out in benzene under argon. The results are summarized in Tables 1 and 2. Although BNAH was converted into unidentified products, a mass balance between starting materials and the sulphoxide or sulphilimine recovered and sulphide formed showed that the reductions are clean with no sulphur-containing by-products. Only sulphoxides which possessed a highly electronegative group (*e.g.* benzoyl or cyano) at the α-carbon underwent both *S*-deoxygenation and *S*-dealkylation (see Table 3). Tosylamine was isolated in undetermined yield from the reaction mixture of BNAH with *N*-tosylsulphilimines.

Dimethyl sulphoxide is known to co-ordinate to TPPFe^{III} to form a high-spin 6-co-ordinate iron(III) porphyrin complex.[17,18] Co-ordination of both sulphoxides and sulphilimines to TPPFe^{III}Cl has been confirmed by the change in the visible spectrum of TPPFe^{III}Cl on the addition of either sulphoxide or sulphilimine. Typical examples are shown in Figures 1 and 2. Further information on the TPPFe^{III} catalysed reduction of sulphoxides was obtained from visible spectral measurements, the colour change during the reaction being remarkable. During the spectral measurements, the reaction of TPPFe^{III}Cl with BNAH in benzene gave an unidentified substance, which was inert to dioxygen and failed to catalyse sulphoxide reduction. A solution of TPPFe^{III}Cl in benzene in the presence of 50 μM BNAH under argon afforded a visible spectrum with $\lambda_{max.}$ at 418, 508, 575, 650, and 688 nm (see Figure 3). This agrees with the spectral data of TPPFe^{III}(BNAH) obtained by the reaction of TPPFe$^{III}ClO_4$ with BNAH in CH_2Cl_2.[19] When the solution was heated at 50 °C for 1 h, the spectrum changed to $\lambda_{max.}$ at 406, 536, and 609 nm but since it was unchanged on introduction of air to the solution, clearly it did not arise from the presence of ferrous complex. However, in the presence of

Table 1. Reduction of sulphoxides by TPPFeCl[a]

Sulphoxide	Reductant[b] (equiv.)	Solvent	Temp. (°C)	Time (h)	Yield of sulphide (%)[c]
Dibenzothiophene oxide	BNAH (1.1)	PhH	80	2	96
	BNAH (1.5)[d]	PhH	80	4	98[d]
	$NaBH_4$	PhH–EtOH	25	3	99
Dibenzodithiin oxide	BNAH (1.5)	PhH	80	15	65
	$NaBH_4$	Diglyme	50	24	55
$PhSOC_6H_4NO_2$-*p*	BNAH (1.5)	PhH	80	18	75
Ph_2SO	BNAH (3.0)	PhH	80	40	38
$PhSOC_6H_4Me$-*p*	BNAH (2.0)	PhH	80	13	43
	$NaBH_4$	Diglyme	50	24	32
2-Pyridyl SOMe	BNAH (2.0)	PhH	80	15	43
	$NaBH_4$	Diglyme	50	24	52
$(PhCH_2)_2SO$	BNAH (3.0)	PhH	80	40	15
	$NaBH_4$	Diglyme	50	40	18

[a] 5 Mol% of $TPPFe^{III}Cl$ to sulphoxide was employed. [b] Mol equiv. to sulphoxide. [c] Isolated yield. [d] The μ-oxo dimer was used as a catalyst.

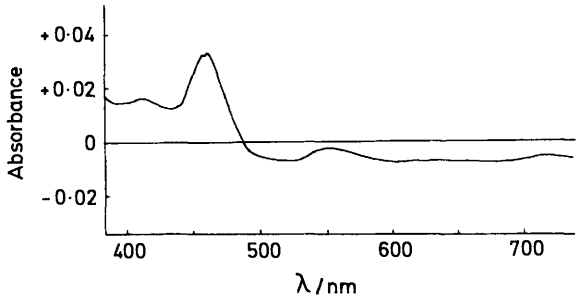


Figure 1. Difference spectrum of $TPPFe^{III}Cl$ in benzene. Reference cuvette, $TPPFe^{III}Cl$ (6μ M); sample curvette, $TPPFe^{III}Cl$ (6 μM) and methyl *p*-tolyl sulphoxide (4.8 mM)

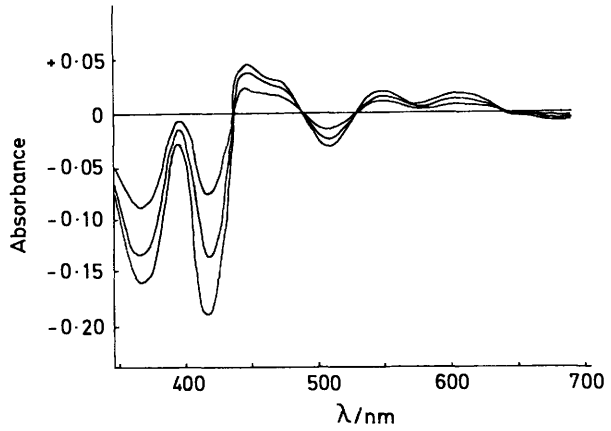


Figure 2. Difference spectra of $TPPFe^{III}Cl$ in benzene. Sample cuvette, $TPPFe^{III}Cl$ (6 μM) and diphenyl sulphilimine (1.0, 2.1, and 3.1 mM) respectively; reference cuvette, $TPPFe^{III}Cl$ (6 μM)

imidazole, $TPPFe^{III}Cl$ was smoothly reduced on treatment with BNAH under argon to $TPPFe^{II}(imidazole)_2$ ($\lambda_{max.}$ at 428, 534, 566, and 609 nm)[20] which reproduced immediately the original spectrum of $TPPFe^{III}(imidazole)_2$ ($\lambda_{max.}$ at 417 and 550 nm) when a solution of the latter was exposed to air (Figure 4). However, since during the reduction of sulphoxides, there was no porphyrin derivative present which is inert to both dioxygen and sulphoxide, regardless of the absence of imidazole, it seems

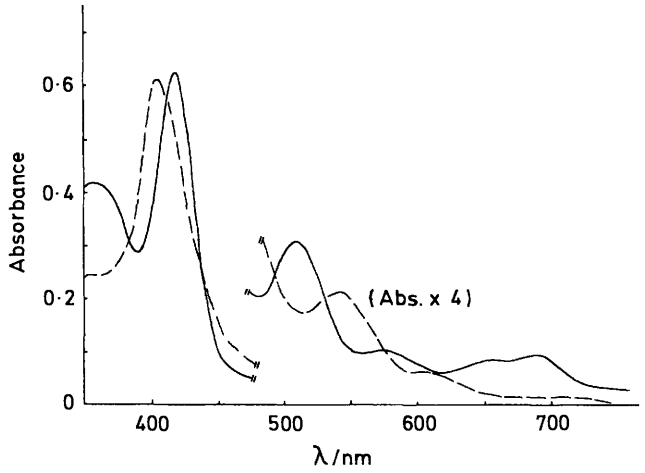


Figure 3. Visible spectra of $TPPFe^{III}Cl$/BNAH reaction mixture in the absence of imidazole in benzene in a degassed and sealed cuvette. The initial solution contained $TPPFe^{III}Cl$ (5 μM) and BNAH (50 μM). Initially $\lambda_{max.}$ = 418, 508, 575, 650, and 688 nm (——); after 1 h at 50 °C, $\lambda_{max.}$ = 406, 536, and 609 nm (- - - -)

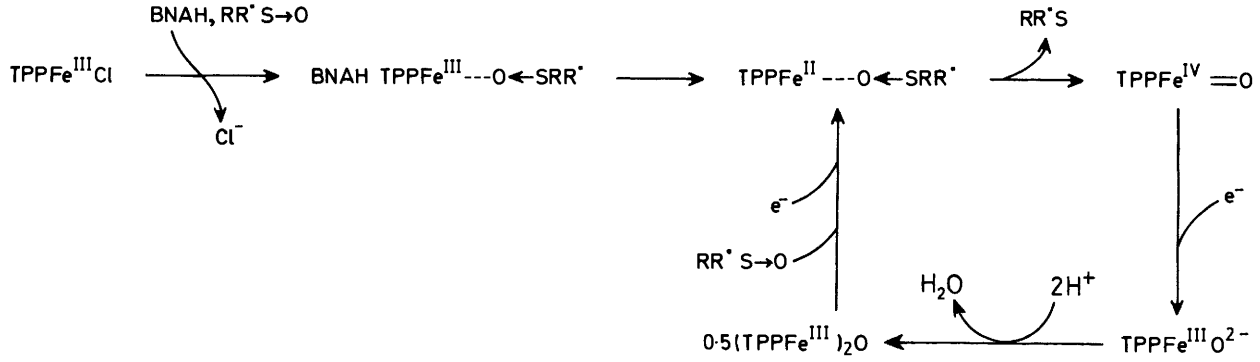
likely that the presence of ligand, such as imidazole, sulphoxide, or sulphilimine *etc.*, prevents the formation of the inactive derivative of TPPFe. The colour change of the TPPFe catalysed sulphoxide reaction mixture from purple to green was used to confirm the formation of the μ-oxo dimer, $(TPPFe^{III})_2O$, by comparing the visible spectrum of the green reaction solution with that of an authentic sample.[21] As illustrated in Figure 5, the μ-oxo dimer can be reduced to $TPPFe^{II}(imidazole)_2$ quantitatively with BNAH in the presence of imidazole under argon. The results suggest that the μ-oxo dimer has a catalytic ability to reduce sulphoxide. Indeed, $(TPPFe^{II})_2O$ was found to promote the reaction as shown in Table 1.

The order of catalytic ability in the reduction of sulphoxides with BNAH for the following metalloporphyrins is the reverse of that expected from the reduction potentials of the three catalysts: $TPPCu^{II}$ < $TPPCo^{II}$ < $TPPFe^{III}$.[16] Hence the rate of the metalloporphyrin catalysed reduction of sulphoxides with BNAH is controlled at least partly by the rate of electron transfer from BNAH to the metal catalyst. On the basis of this assumption, the $TPPFe^{III}$ catalysed reduction of sulphoxides and sulphilimines will be accelerated by replacing BNAH with a reducing agent with a greater ability to reduce $TPPFe^{III}$. Thus,

Table 2. Reduction of sulphilimines catalysed by $TPPFe^{III}$ [a]

Sulphilimine	Reductant (equiv.)[b]	Solvent	Temp. (°C)	Time (h)	Yield of sulphide (%)[c]
Ph_2SNTs	BNAH (2.0)	PhH	80	1	96
	$NaBH_4$	PhH–EtOH	25	1.5	94
p-TolylS(Me)NTs	BNAH	PhH	80	1	93
$(PhCH_2)_2SNTs$	BNAH (2.0)	PhH	80	1	89
	BNAH (5.0)[d]	PhH	25	12	Trace
	BNAH (1.1)	PhH	25	1	88
Ph_2SNTs	$NaBH_4$[d]	EtOH	25	1.5	6
	$NaBH_4$	PhH–EtOH	25	0.1	98
	$NaBH_4$[e]	PhH–EtOH	25	1	83
o-$MeOC_6H_4$(Ph)NTs	BNAH (1.5)	PhH	25	1.5	92
	$NaBH_4$	PhH–EtOH	25	0.2	96
p-ClC_6H_4S(Ph)NTs	BNAH (1.1)	PhH	25	0.25	95
	$NaBH_4$	PhH–EtOH	25	0.1	95
p-$NO_2C_6H_4$S(Ph)NTs	BNAH (1.95)	PhH	25	0.1	98
	$NaBH_4$	PhH–EtOH	25	0.1	97

[a] 5 Mol% of $TPPFe^{III}Cl$ to sulphilimine was used. [b] Mol equiv. to sulphilimine. [c] Isolated yield. [d] Without catalyst. [e] $TPPCo^{II}$ Was used as catalyst.



Scheme 3.

the $TPPFe^{III}$ catalysed reductions of both sulphoxides and sulphilimines were carried out with $NaBH_4$, a more powerful reducing agent than BNAH (see Tables 1 and 2). In fact, the $TPPFe^{III}$ catalysed reduction of sulphoxides with $NaBH_4$ appeared to proceed faster than that with BNAH. The observation that an increase in electronegativity of the *S*-substituent accelerates the rate of the $TPPFe^{III}$ catalysed reduction of both sulphoxides and sulphilimines seems to indicate that heterolytic cleavage of either sulphoxides or sulphilimines to afford the sulphides also partly controls the rate of steady-state catalytic reactions. All these experimental results may be explained by the mechanism shown in Scheme 3. The first step involves the co-ordination of the substrate to the iron catalyst. Since the co-ordination of the sulphoxide shifts the reduction potential of $TPPFe^{III}$ to the anodic side,[17] the single electron-transfer may take place from BNAH to Fe^{III} in the ternary ferric complex affording the Fe^{II} intermediate. Heterolytic cleavage of the S–O bond of the sulphoxide attached to the Fe^{II} then affords the sulphide and ferryl oxenoid intermediates which accept a single electron from BNAH or another reducing species such as BNA$^{\bullet}$ *etc.* to regenerate the ferric intermediate. This mechanism may be supported by the fact that a sulphoxide-bearing electron-accepting group accelerates the reaction and that $TPPFe^{II}$ reacts very readily with tertiary amine *N*-oxides to generate $TPPFe^{IV}=O$.[22] $TPPFe^{III}O^{2-}$ Would combine with other TPP-Fe^{III} species to afford the μ-oxo dimer $[(TPPFe^{III})_2O]$ which then regenerates the intermediate $[TPPFe^{II}O–SRR^{\bullet}]$ upon reaction with BNAH and sulphoxide, as previously mentioned.

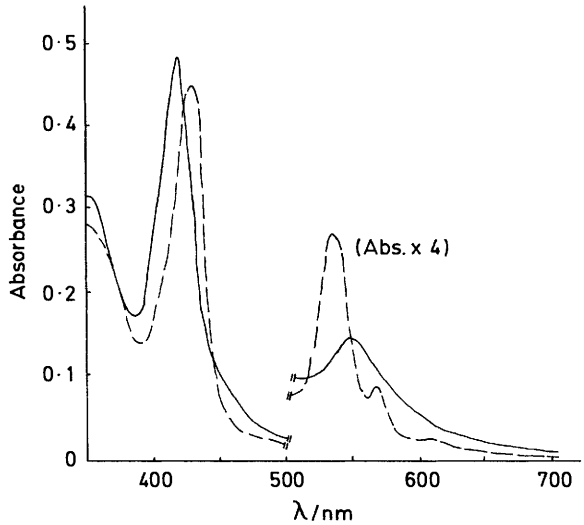


Figure 4. Visible spectral change for the $TPPFe^{III}Cl$/BNAH reaction mixture in benzene in the presence of imidazole. Initially $\lambda_{max.}$ = 417 and 550 nm (——). After reaction for 1 h at 50 °C, $\lambda_{max.}$[$TPPFe^{II}$-$(Im)_2$] = 428, 534, 566, and 609 (– – – –)

The reaction of *N*-tosylsulphilimines proceeds much more readily than that of the corresponding sulphoxide (Table 2). *N*-Unsubstituted sulphilimines are extremely reactive towards

Table 3. Reductive cleavage of S–C bonds with $TPPFe^{III}Cl$/BNAH in benzene at 80 °C under argon[a]

Substrate	Time (h)	Products (yield %)		
p-TolSOCH$_2$COPh	4	*p*-TolCH$_2$COPh (72)	(*p*-TolS)$_2$ (21)	PhCOMe (18)
p-TolSCH$_2$COPh	4	(*p*-TolS)$_2$ (28)	PhCOMe	
p-TolSOCH$_2$CN	5	*p*-TolSCH$_2$CN (60)	(*p*-TolS)$_2$ (31)	
p-TolSCH$_2$CN	5	(*p*-TolS)$_2$ (19)		

[a] 5 Mol% of $TPPFe^{III}Cl$:substrate. 1.2 Mol equiv. of BNAH:substrate.

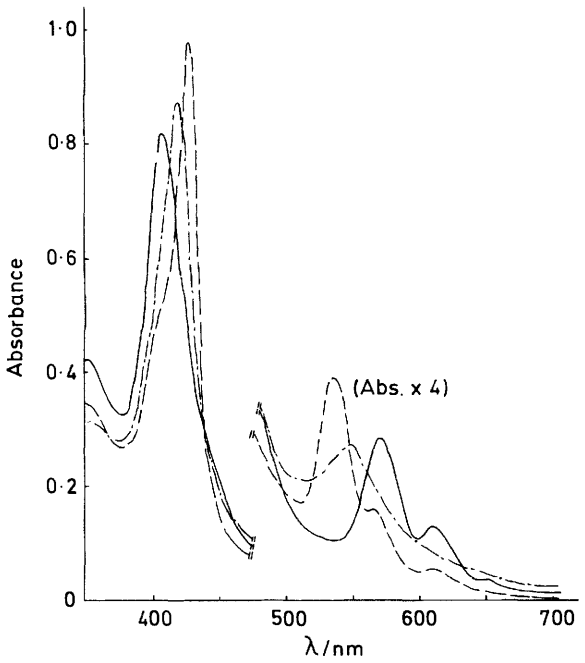
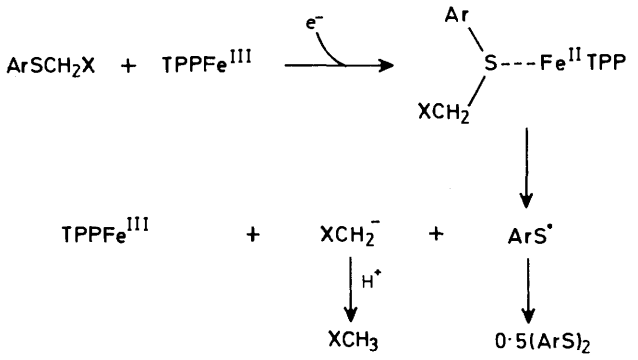


Figure 5. Visible spectral change during the reaction between $(TPPFe^{III})_2O$ and BNAH in the presence of imidazole in benzene in a sealed and degassed cuvette. Initial concentration of $[(TPPFe^{III})_2O]$ and imidazole was 3.5 μM and 3.5 mM respectively. Initially, $\lambda_{max.}$-$[(TPPFe^{III})_2O]$ = 408, 571, and 612 nm (——). After 3 h, $\lambda_{max.}$-$[TPPFe^{II}(Im)_2]$ = 426, 535, 565, and 610 nm (– – – –). The reaction mixture containing $TPP^{II}(Im)_2$ was exposed to the air ($\lambda_{max.}$ = 317 and 510 nm) (– · – · –)

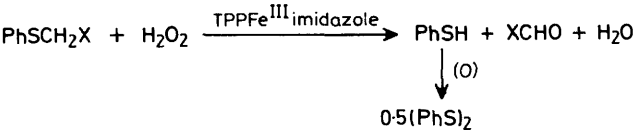
the $TPPFe^{III}$/BNAH system and reduction was complete within 1.5 h even at room temperature (Table 2). Thus, the rate of reduction of these semipolar bonds by the $TPPFe^{III}$/BNAH system decreases in the order: *N*,*N*-dimethylaniline *N*-oxide[22] > *N*-unsubstituted sulphilimines > *N*-tosylsulphilimines > sulphoxides. This order of reactivity follows the increasing bond of these semipolar bonds.

Reductive Cleavage of S–C *Bonds.*—It is interesting to note that the reduction of phenacyl *p*-tolyl sulphoxide and cyanomethyl *p*-tolyl sulphoxide with the $TPPFe^{III}$/BNAH system gave reductive S–C bond cleavage products in addition to the normal reduction products, *i.e.* the sulphides (see Table 3). The results of control experiments (Table 3) shows that S–C bond cleavage takes place only when the α-carbon possesses highly electron-withdrawing groups, such as benzoyl and cyano. The *p*-nitrophenyl group is not sufficiently electronegative to promote the reductive cleavage of the S–C bond; this cleavage may be best explained by the single electron-transfer mechanism proposed for the reductive cleavage of the C–Cl bonds (Scheme 4).[23]



Scheme 4.

Thus, $TPPFe^{III}Cl$ has been found to catalyse both the reductive and the oxidative *S*-dealkylation[24] of particular sulphides which bear highly electronegative groups at the α-carbon (Scheme 5).



Scheme 5.

Experimental

M.p.s were measured on a Yanako instrument and were uncorrected. Electronic spectra were recorded on a Hitachi 260-50 spectrophotometer. Liquid chromatography was performed on a Japan Analytical Industry LC-9 equipped with a JAIGEL 1H column (1 m) or a Hitachi 638-50 instrument equipped with a Hitachi gel #3011 column (0.5 m).

Materials.—1-Benzyl-1,4-dihydronicotinamide was prepared according to the method of Mauzerall and Westheimer.[25] *meso*-Tetraphenylporphinatoiron(III) chloride and μ-oxo-bis[tetraphenylporphinatoiron(III)] were synthesized by literature procedures.[26] *meso*-Tetraphenylporphinatocobalt(II) and *meso*-tetraphenylporphinatocopper(II) were also synthesized by literature procedures.[27]

Sulphoxides. Dibenzyl sulphide was purchased from the Wako Pure Chemicals Co. and recrystallised before use. All sulphoxides were prepared by oxidation of the corresponding sulphides by H_2O_2 or *m*-chloroperbenzoic acid and purified by recrystallisation or distillation. The following compounds were prepared in this way: dibenzothiophene, m.p. 186—187.5 °C (lit.,[28] 188.5 °C); thianthrene mono-oxide, m.p. 143—143.5 °C (lit.,[29] 143 °C); methyl 2-pyridyl sulphoxide, b.p. 117 °C/6 mmHg (lit.,[30] 117 °C/6 mmHg); phenyl *p*-tolyl sulphoxide, m.p. 68.5—69.5 °C (lit.,[31] 69—70 °C); phenyl *p*-nitrophenyl sulphoxide, m.p. 107 °C (lit.,[32] 106—107 °C); and diphenyl sulphoxide, m.p. 69—70 °C (lit.,[29] 69—71 °C).

Sulphilimines. *N*-Tosylsulphilimines were prepared by treating the corresponding sulphide with chloramine-T.[32] *N*-Unsubstituted sulphilimines were obtained by treating the corresponding *N*-tosylsulphilimines with conc. sulphuric acid.[33] The following compounds were prepared in this way: *p*-tolyl methyl *N*-tosylsulphilimine, m.p. 124—125 °C (lit.,[32]

125—127 °C); dibenzyl *N*-tosylsulphilimine, m.p. 190 °C (lit.,[32] 190—191 °C); diphenyl *N*-tosylsulphilimine, m.p. 111—112 °C (lit.,[34] 111—112 °C); diphenyl sulphilimine, m.p. 74 °C (lit.,[33] 74 °C); phenyl-2′-methoxyphenyl sulphilimine, m.p. 98—99 °C (lit.,[35] 96—97 °C); phenyl 4′-chlorophenyl sulphilimine, m.p. 46—47 °C (lit.,[33] 48—49 °C); and phenyl 4′-nitrophenyl sulphilimine, m.p. 107 °C (lit.,[33] 98—99 °C).

Reaction of Sulphoxides with the $TPPFe^{III}Cl$/BNAH *System.*—An aliquot of the sulphoxide (1.0 mmol) was treated with BNAH (1.1 mmol) and $TPPFe^{III}Cl$ (0.05 mmol) in dry benzene (5 ml) at 80 °C under argon. The progress of the reaction was monitored by t.l.c. (silica gel; $CHCl_3$) or liquid chromatography. After the disappearance of the sulphoxide, the reaction mixture was concentrated under reduced pressure. The residue was column-chromatographed (silica gel) with hexane as eluant. Evaporation of the solvent gave the pure sulphide. All the sulphides were identified by comparing l.c. retention times and i.r. spectra with those of authentic samples. The reduction catalysed by other metalloporphins involving $TPPCu^{II}$, $TPPCo^{II}$, and $(TPPFe^{III})_2O$ has been carried out according to the above procedure.

Reaction of Sulphilimines with the $TPPFe^{III}Cl$/BNAH *System.*—A mixture of sulphilimines (1.0 mmol), BNAH (1.05—1.11 mmol), $TPPFe^{III}Cl$ (0.05 mmol), and dry benzene (10 ml) was stirred at room temperature under argon, and the reaction was monitored by t.l.c. (silica gel; benzene–ethanol) or liquid chromatography. The reaction mixture was given the same work-up as above.

Reaction of Sulphoxides with the $TPPFe^{III}Cl/NaBH_4$ *System.—Method A.* Dibenzothiophene oxide (1 mmol) and $TPPFe^{III}Cl$ (0.05 mmol) were dissolved in dry benzene (5 ml) at room temperature under argon and the whole solution was stirred with a magnetic stirrer. $NaBH_4$ (1.5 mmol) dissolved in EtOH (2 ml) was added to the solution and the reaction was monitored by t.l.c. (silica gel; $CHCl_3$). After 3 h, when the reaction was complete ethyl acetate was added to the mixture to destroy excess $NaBH_4$. The reaction mixture was concentrated under reduced pressure and column-chromatographed (silica gel; hexane). After evaporation of the solvent, dibenzothiophene (99%) was obtained.

Method B. A solution of sulphoxide (1.0 mmol), $TPPFe^{III}Cl$ (0.05 mmol), and $NaBH_4$ (1.5 mmol) in diglyme (5 ml) was stirred at 50 °C under argon. Subsequent treatment followed the method outlined in Method A.

Reaction of Sulphilimines with the $TPPFe^{III}Cl/NaBH_4$ *System.*—The procedure was similar to Method A outlined above.

Spectral Analysis of the Reaction Between $TPPFe^{III}Cl$ *and* BNAH.—A typical example is as follows. A solution of $TPPFe^{III}Cl$ in benzene (5 μM; 3.0 ml) containing imidazole (5 mM) was pipetted into a two-necked flask. One arm was connected to a u.v. cuvette; the other was connected to a small tube containing BNAH (0.075 μmol). The vessel was joined to a vacuum line and degassed by repeated freeze–thaw cycles (pumping by diffusion pump). The vessel was sealed by burner. The BNAH was then dissolved in the benzene solution and the whole was transferred into a u.v. cuvette. The cuvette was sealed and placed in a spectrophotometer to record the visible spectrum of the mixture. After 1 h at 50 °C in the dark, the spectrum of $TPPFe^{II}(imidazole)_2$ was recorded.

References

1 C. C. Price and S. Oae, 'Sulphur Bonding,' Ronald Press, New York, 1962; S. Oae, 'Chemistry of Organosulphur Compounds,' Kagakudojin, Kyoto, 1969, vol. 2; S. Oae, 'Organic Chemistry of Sulphur,' Plenum Press, New York, 1977; S. Oae, 'Organic Sulphur Chemistry,' Tokyokagakudojin, Tokyo, 1982.
2 S. M. Benson, *Chem. Rev.*, 1978, **78**, 23.
3 J. Drabowicz, T. Numata, and S. Oae, *Org. Prep. Proced. Int.*, 1977, **9**, 63; J. Drabowitz, H. Togo, M. Mikolajczyk, and S. Oae, *ibid.*, 1984, **16**, 173; S. Oae and H. Togo, *Chemistry* (*Kagaku*), 1982, **37**, 812 (*Chem. Abstr.*, 1983, **98**, 16023u).
4 S. Oae and N. Furukawa, 'Chemistry of Sulphilimines and Related Derivatives,' ACS Research Monograph, 1983.
5 S. Tamagaki, M. Mizuno, H. Yoshida, H. Hirota, and S. Oae, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2456; J. Drabowicz and S. Oae, *Synthesis*, 1977, 404.
6 S. Oae, A. Nakanishi, and N. Tsujimoto, *Tetrahedron*, 1972, **28**, 2981; S. Oae, T. Yagihara, and T. Okabe, *ibid.*, 1972, **28**, 3203; J. Drabowicz and S. Oae, *Chem. Lett.*, 1977, 767; T. Numata, H. Togo, and S. Oae, *ibid.*, 1979, 329.
7 D. C. Wood and S. W. Jacob, *Quart. Reps. on Sulfur Chem.*, 1968, **3**, 159, and references cited therein.
8 V. Distefano and H. H. Borgstedt, *Science*, 1964, **144**, 1137.
9 T. Meshi, M. Yoshikawa, and Y. Saito, *Biochem. Pharmacol.*, 1970, **19**, 1351.
10 R. C. Doney and J. F. Thompson, *Biochim. Biophys. Acta*, 1966, **124**, 39.
11 S. Black, E. M. Harte, B. Hudson, and L. Wartfsky, *J. Biol. Chem.*, 1960, **235**, 2910.
12 S. Kitamura, K. Tatsumi, and H. Yoshimura, *J. Pharm. Dyn.*, 1980, **3**, 290; S. Kitamura, K. Tatsumi, Y. Hirata, and H. Yoshimura, *ibid.*, 1981, **4**, 528.
13 A. Ohno, H. Yamamoto, and S. Oka, *J. Am. Chem. Soc.*, 1981, **103**, 2041; A. Ohno and N. Kito, *Chem. Lett.*, 1972, 39; S. Yasui, K. Nakamura, A. Ohno, and S. Oka, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 196.
14 S. Fukuzumi, N. Nishizawa, and T. Tanaka, *J. Org. Chem.*, 1984, **49**, 3571; S. Fukuzumi, S. Koumitsu, K. Hironaka, and T. Tanaka, *J. Am. Chem. Soc.*, 1987, **109**, 305.
15 K. Fujimori, H. Togo, Y. Perchers, N. Nagata, N. Furukawa, and S. Oae, *Tetrahedron Lett.*, 1985, **26**, 775.
16 T. Nagata, T. Yoshimura, K. Fujimori, and S. Oae, *Tetrahedron Lett.*, 1984, **25**, 341.
17 L. A. Constant and D. G. Davis, *Anal. Chem.*, 1975, **47**, 2253.
18 M. Zorist and G. N. LaMar, *J. Am. Chem. Soc.*, 1978, **100**, 1944; D. L. Budd, G. N. LaMar, K. C. Langry, K. M. Smith, and R. Nayyir-Mazhir, *ibid.*, 1979, **101**, 6091.
19 S. Fukuzumi, Y. Kondo, and T. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1985, 1053.
20 J. P. Collman and C. A. Reed, *J. Am. Chem. Soc.*, 1973, **95**, 2043; D.-H. Chin, G. N. La Mar, and A. L. Balch, *J. Am. Chem. Soc.*, 1980, **102**, 5945.
21 E. B. Fleischer and T. S. Srvastava, *J. Am. Chem. Soc.*, 1969, **91**, 2403.
22 K. Fujimori, S. Fujiwara, T. Takata, and S. Oae, *Tetrahedron Lett.*, 1986, **27**, 581.
23 R. S. Wade and C. E. Castro, *J. Am. Chem. Soc.*, 1973, **95**, 231.
24 S. Oae, Y. Watanabe, and K. Fujimori, *Tetrahedron Lett.*, 1982, **23**, 1189.
25 D. Mauzrall and F. M. Westheimer, *J. Am. Chem. Soc.*, 1955, **77**, 2261.
26 A. D. Alder, F. R. Longo, J. D. Finareli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476; A. D. Alder, F. R. Longo, and V. Varadi, *Inorg. Synth.*, 1976, **16**, ch. 7; G. M. Badger, R. A. Jones, and R. L. Laslett, *Aust. J. Chem.*, 1964, **17**, 1028.
27 V. M. Albers and H. V. Knorr, *J. Chem. Phys.*, 1941, **9**, 1941.
28 S. Oae, S. Makino, and Y. Tsuchida, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 650.
29 S. Oae, Y. Ohnishi, S. Kozuka, and W. Tagaki, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 364.
30 J. Drabowitz, W. Midura, and M. Mikolajczyk, *Synthesis*, 1979, 39.
31 S. Oae, K. Sakai, and N. Kunieda, *Bull. Chem. Soc. Jpn.*, 1979, **42**, 1964.
32 K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, *Bull. Chem. Soc. Jpn.*, 1979, **42**, 2631.
33 T. Yoshimura, T. Omata, N. Furukawa, and S. Oae, *J. Org. Chem.*, 1976, **41**, 1278.
34 A. Nakanishi and S. Oae, *Chem. Ind.*, 1971, 960.
35 M. Moriyama, T. Yoshimura, N. Furukawa, T. Numata, and S. Oae, *Tetrahedron*, 1976, **32**, 3003.

Received 15*th August* 1988; *Paper* 8/03308K