Model Systems for Cytochrome P450 Dependent Mono-oxygenases. Part 1. Oxidation of Alkenes and Aromatic Compounds by Tetraphenylporphinatoiron(III) Chloride and Iodosylbenzene

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A selection of aliphatic alkenes, substituted styrenes, and *cis*- and *trans*-stilbene have been epoxidised with tetraphenylporphinatoiron(III) chloride and iodosylbenzene, a model system for the cytochrome P450 dependent mono-oxygenases. The epoxidations are stereospecifically *syn* and the reactivities of the alkenes show that *cis*-alkenes are more reactive than their *trans*-isomers and that electron-releasing substituents favour the reaction. A Hammett ρ value of -0.93 is obtained from the epoxidation of the substituted styrenes. Three polycyclic hydrocarbons, phenanthrene, acenaphthylene, and pyrene, are epoxidised in low yield. The model system hydroxylates anisole and naphthalene but is insufficiently reactive to oxidise benzene; with toluene, side-chain oxidation but no ring hydroxylation occurs. The mechanisms of these oxidations and the nature of the reactive species are discussed.

CURRENTLY there is much interest in the mechanisms of the many oxygenations brought about by the cytochrome P450 mediated mono-oxygenases.[1] In particular, this has centred on the mechanisms of aromatic and aliphatic hydroxylation, alkene epoxidation [1a,f,2] and on the nature of the active oxidant that is capable of performing these oxygenations.[1,2b,d] To this end a number of model systems have been studied to build up a mechanistic framework of the possible oxidative pathways to help delineate the mechanisms of the biological processes.

In the past our work has concentrated largely on the mechanisms of aromatic hydroxylation [3] although the importance of the other oxidations brought about by the mono-oxygenases has led us to extend our studies to include these processes.[4]

It is generally agreed that the initial step in the oxidation of C=C bonds, both in alkenes and aromatic compounds, by cytochrome P450 mediated mono-oxygenases is oxygen transfer to give an epoxide.[1a,2a,b,e,5] Subsequent hydration (epoxide hydratase), conjugation (glutathione *S*-transferase), and non-enzymic rearrangement lead to the products typically found in the *in vivo* metabolism of these compounds. However, the nature of the active oxidant and whether the epoxidation is a two-step radical process or a concerted ionic one remain areas of active discussion and research.[1,2] In this paper we report on mechanistic aspects of alkene epoxidation and to a lesser extent aromatic hydroxylation by a model system, first described by Groves and his co-workers,[6] involving tetraphenylporphinatoiron(III) chloride ($Fe^{III}TPPCl$) and iodosylbenzene. The active oxidant in this model system is thought to bear a close resemblance to that in the enzymic process [1f] and in particular to that present in the anaerobic *in vitro* systems where the dioxygen and NADPH are replaced by chemical oxidants such as iodosylbenzene [7] and hydroperoxides.[8]

RESULTS AND DISCUSSION

Epoxidation of Alkenes.—A solution of $Fe^{III}TPPCl$ in dichloromethane brings about the quantitative conversion of iodosylbenzene into iodobenzene and, depending on the structure and reactivity of the substrate, can concomitantly catalyse an efficient transfer of the oxygen to the alkenic C=C bond. Table 1 records the products and yields from the oxidation of seven aliphatic alkenes, *cis*- and *trans*-stilbene, and some substituted styrenes by the model system. The data reported here are in broad agreement with the views of Groves and his co-workers that the $Fe^{III}TPPCl$ and iodosylbenzene generate an active oxidant which can be trapped by the substrate in competition with the self-oxidation and destruction of the iron porphyrin.[1f] The epoxidation yields range from 7 to 89% and reveal that, in general, the more electron rich the alkene the better it competes for the oxidant and the higher the yield of epoxide. Thus the yields of the epoxides give an approximate measure of the relative reactivities of the substrates towards the oxidising species.

Relative Reactivities of the Alkenes towards Epoxidation by the Model System.—Relative reactivities were obtained from competition experiments and, for the aliphatic alkenes, these show an overall difference in reactivity of *ca.* 200-fold between the terminal alkene oct-1-ene and the fully methylated alkene 2,3-dimethylbut-2-ene (Table 2). The overall order of reactivities depends on a combination of electronic and steric effects, thus although the reactivities of all the dialkylated alkenes lie between the tri- and mono-alkylated compounds there is a difference of 14-fold between *cis*- and *trans*-4-methylpent-2-ene. The greater reactivity of *cis*-alkenes over their *trans*-isomers with this epoxidising system has been reported before by Groves and his co-workers.[6,9] The order and range of reactivities could be accounted for by the oxidant being either a reactive electrophile, an electrophilic radical, or an oxenoid species. For comparison the relative reactivities of some alkenes towards a selection of species are given in Table 3.

The relative reactivity of two alkenes, cyclohexene and 1-methylcyclohexene, was monitored during the course of the oxidation. This experiment was carried out at the lower temperature of -10 °C to slow down the reaction and thus increase the number of measurements. The reactivity of 1-methylcyclohexene relative to cyclohexene, monitored at 1, 8, 16, and 24 min and after the reaction was complete at 45 min, remained constant throughout the reaction at 5.5 ± 0.3. As expected the difference in reactivity between the two substrates increases with a decrease in temperature.

Since the relative rate data from this study are complicated by the fact that the differences in rates arise from a combination of steric and electronic effects, we examined the relative reactivities of some 3- and 4-substituted styrenes to obtain the influence of electronic effects, free from variations in steric hindrance (Table 4).

TABLE 1

The epoxidation of alkenes by Fe^{III}TPPCl and iodosylbenzene in dichloromethane at room temperature: yields based on iodosylbenzene consumed

Substrate	Product	Yield (%)
2,3-Dimethylbut-2-ene	2,3-Epoxy-2,3-dimethylbutane	89
2-Methylbut-2-ene	2,3-Epoxy-2-methylbutane	74
1-Methylcyclohexene	1,2-Epoxy-1-methylcyclohexane	61
cis-4-Methylpent-2-ene	*cis*-2,3-Epoxy-4-methylpentane	51
trans-4-Methylpent-2-ene	*trans*-2,3-Epoxy-4-methylpentane	13
	2-Methylpent-3-en-2-ol } 4-Methylpent-2-en-1-ol }	2
Cyclohexene	Epoxycyclohexane	48
	Cyclohex-2-enol	13
Oct-1-ene	1,2-Epoxyoctane	7
	Oct-1-en-3-ol	1
cis-Stilbene	*cis*-Stilbene epoxide	52
trans-Stilbene	*trans*-Stilbene epoxide	2
4-Methoxystyrene	4-Methoxystyrene epoxide	71
4-Methylstyrene	4-Methylstyrene epoxide	45
Styrene	Styrene epoxide	32
4-Chlorostyrene	4-Chlorostyrene epoxide	30
3-Chlorostyrene	3-Chlorostyrene epoxide	24
4-Nitrostyrene	4-Nitrostyrene epoxide	16

TABLE 2

The reactivities of aliphatic alkenes, relative to oct-1-ene, towards epoxidation by Fe^{III}TPPCl and iodosylbenzene in dichloromethane at room temperature

Substrate	Reactivity relative to oct-1-ene
2,3-Dimethylbut-2-ene	204
1-Methylcyclohexene	84
2-Methylbut-2-ene	76
cis-4-Methylpent-2-ene	28
Cyclohexene	20
trans-4-Methylpent-2-ene	2
Oct-1-ene	1

TABLE 3

Relative reactivities of alkenes towards carbenes, radicals, and electrophiles

Substrate	Reactant			
	$:CCl_2$ [10]	$\cdot CCl_3$ [11]	Br_2 [12]	CH_3CO_3H [13]
2,3-Dimethylbut-2-ene	285		10^4	
2-Methylbut-2-ene	124	0.9	10^3	196
2-Methylpropene	44.6	5.2		18.4
cis-Pent-2-ene	11.3		50 }	18.6
trans-Pent-2-ene	8.6		4.3 }	
Cyclohexene	5.4	0.2		25.8
Alk-1-ene	1.0 *	1.0 †	1.0 ‡	1.0 †

* Hex-1-ene. † Oct-1-ene. ‡ But-1-ene.

As expected, electron-donating substituents enhance the rate of epoxidation. A Hammett treatment of the data gives a good linear correlation against σ^+ and a least mean squares analysis gives a ρ value of -0.93 ± 0.05 (Figure). This ρ value is within the range of values for the epoxidation of styrenes and stilbenes by peracids [14] and by t-butyl hydroperoxide with a molybdenum catalyst.[15] The better correlation of the relative rate data with σ^+ than with σ and the sign and size of the ρ value are in agreement with the attacking species being electrophilic and the development of positive charge on the α-carbon of the styrene in the transition state for epoxidation. Hanzlik and Shearer come to a very similar conclusion about the nature of the transition state in the peracid epoxidation of styrenes.[16]

TABLE 4

The reactivities of substituted styrenes, relative to styrene, towards epoxidation by Fe^{III}TPPCl and iodosylbenzene in dichloromethane at room temperature

Substrate	Reactivity relative to styrene
4-Methoxystyrene	6.61
4-Methylstyrene	2.38
Styrene	1.00
4-Chlorostyrene	0.98
3-Chlorostyrene	0.49
4-Nitrostyrene	0.24

The kinetic selectivity for *cis*-alkenes over their *trans*-isomers resembles that observed by Keay and Hamilton [17] for the epoxidation of *cis*- and *trans*-hex-3-ene by intermediates formed in the reaction of but-2-yne and ozone, but is in marked contrast to some other epoxidising systems. Thus the rate of epoxidation of *cis*-hex-3-ene relative to that of the *trans*-isomer is 1.0 with the palladium(II) acetate–azibenzil–dioxygen system [18] and 1.4 with peroxybenzimidic acid.[19] Simple free radicals, such as hydroxyl,[20] peroxyacetyl,[21] and methyl radicals [22] and O(^3P) atoms,[23] show a preference

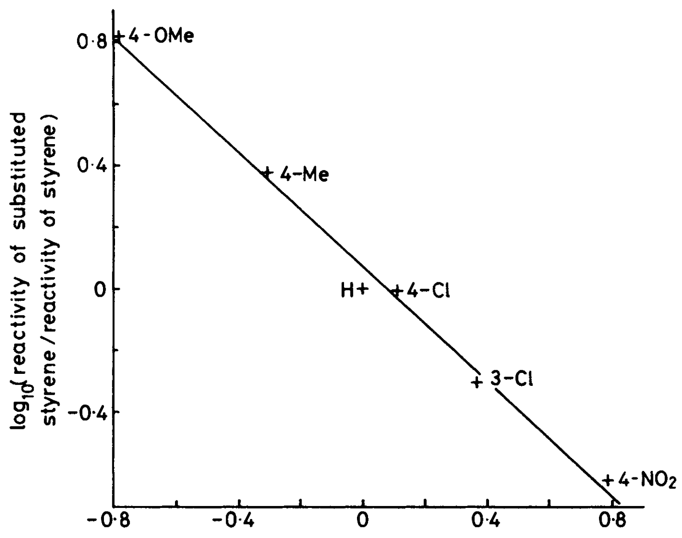


FIGURE Plot of $\log_{10}$ (relative reactivity of substituted styrene to styrene) against σ^+ values of substituents

for the *trans*-isomer. Groves and his co-workers interpret the much greater reactivity of the *cis*-diastereoisomers as arising from steric hindrance giving a greater accessibility of the *cis*-alkene to the active oxidant on the porphyrin. Keay and Hamilton [17] use a similar argument to account for their results.

Epoxidation by the model system is stereospecifically *syn*. The analytical method (g.c. or h.p.l.c.) would have detected the presence of <0.2% of the other epoxide diastereoisomer. The *syn*-addition resembles the stereochemistry of the peracid [24] and molybdenum–t-butyl hydroperoxide [25] epoxidations.

Epoxidation of Polycyclic Aromatic Hydrocarbons.—The mildness of the epoxidising system and the absence of acids and bases in the reaction mixture led us to explore its application to the direct epoxidation of some polycyclic aromatic hydrocarbons. The direct epoxidation of these aromatic compounds has been achieved with a number of oxidising systems [26] of which the most successful are those employing peracids.[26a–c] For this study we selected three compounds with a structural similarity to *cis*-stilbene, namely phenanthrene, pyrene, and acenaphthylene. For each polycyclic aromatic compound the model gave one epoxide (Table 5) and although all the yields were low all the iodosylbenzene was consumed and no other products from the polycyclic compounds were detected. The epoxides were isolated by preparative h.p.l.c. and for phenanthrene 9,10-epoxide and acenaphthylene 1,2-epoxide were characterised by comparison of their spectra with those from authentic materials. Pyrene 4,5-epoxide was identified by comparison of its spectral data with literature values.[27]

TABLE 5

Epoxidation of polycyclic aromatic hydrocarbons by Fe^{III}TPPCl and iodosylbenzene in dichloromethane at room temperature: yields based on iodosylbenzene consumed

Substrate	Product	Yield (%)
Phenanthrene	Phenanthrene 9,10-epoxide	3
Acenaphthylene	Acenaphthylene 1,2-epoxide	15
Pyrene	Pyrene 4,5-epoxide	7

Hydroxylation of Anisole and Naphthalene.—With monocyclic aromatic compounds there is no reaction unless they are sufficiently reactive to compete effectively with the iron porphyrin for the active oxidant. Benzene is not oxidised and toluene gives a low yield of products from side-chain oxidation, benzyl alcohol and benzaldehyde, but none from attack on the aromatic ring (Table 6). However, the more electron rich aromatic compounds anisole and the bicyclic compound naphthalene give small yields of the ring hydroxylated products, 2- and 4-methoxyphenol and 1-naphthol respectively (Table 6).

TABLE 6

The oxidation of toluene, anisole, and naphthalene by Fe^{III}TPPCl and iodosylbenzene in dichloromethane at room temperature: yields based on iodosylbenzene consumed

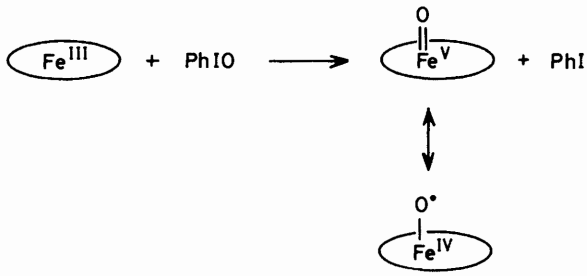
Substrate	Yield of oxidation products (%)	Products	Product distribution (%)
Toluene	0.9	Benzyl alcohol	22
		Benzaldehyde	78
		Cresols	0
Anisole	0.2	2-Methoxyphenol	21
		3-Methoxyphenol	0
		4-Methoxyphenol	62
		Phenol	17
Naphthalene	5	1-Naphthol	100
		2-Naphthol	0

NIH Shift Values from Hydroxylation of Deuteriated Aromatic Compounds.—[4-^{2}H]Anisole (84.7% $^2H_1$) and [1,4-$^2H_2$]naphthalene (95.5% $^2H_2$, 4.5 $^2H_1$) were used to measure the value of the NIH shift in these oxidations. Analysis (g.c.–m.s.) of the 4-methoxyphenol and the trimethylsilyl ether of 1-naphthol give NIH shift values of 68 and 62%, respectively. Very recently Chang and Ebina [28] have reported a value of 60% for the NIH shift from [4-^{2}H]anisole using this system. They have also shown that the yield of aromatic hydroxylation can be increased by using tetrakis(pentafluorophenyl)porphinatoiron(III) chloride in place of Fe^{III}TPPCl. With this modified model system the magnitude of the NIH shift we have obtained from [1,4-$^2H_2$]naphthalene is 69% (Chang and Ebina quote a value of 68% for the NIH shift from [4-^{2}H]anisole with their modified system).

The phenolic isomer distribution and the magnitude of the NIH shifts are in agreement with an arene oxide intermediate which rearranges to phenols *via* cationic species,[1a,2b] or the direct formation of the cationic species.

Allylic Oxidations.—With some substrates the oxidation mixtures contained small yields of products from reaction at saturated allylic and benzylic C–H bonds. In this respect it is important to note that iron porphyrins are catalysts for autoxidation.[29] However, we conclude that none of the saturated C–H bond oxidations in this study arose from autoxidation since the product distributions from autoxidation are very different from those reported here [29a] and carrying out the reactions under nitrogen had no effect on any of the product yields.

Mechanism of Epoxidation and the Nature of the Oxidising Species.—The evidence from this study and from the work of Groves and his co-workers, on the mechanism of oxidation of C=C bonds, can be rationalised in terms of the active oxidant in this model system being an oxoiron intermediate (1) [reaction (1)] which transfers oxygen by a concerted process [reaction (2)], similar to those of peracids, rather than by the radical mechanisms observed with the tetraphenylporphinatomanganese(III) derivatives–iodosylbenzene system [30] and with other oxidants.[17,21,31] Thus peracids and the model system both bring about stereospecific *syn*-epoxidation,[24] involve electrophilic attacking species of similar activity (as assessed from relative reactivity data),[14] show large values for the NIH shift [32] and can be used for the direct epoxidation of polycyclic aromatic hydrocarbons.[26a-c] However, it is not possible to rule out a mechanism that involves two one-electron steps by an electrophilic radical in a solvent cage [33] in which the intermediate (2) is short-lived and is unable to change its stereochemistry by rotation about the central C–C bond before ring closure occurs to give the epoxide [reaction (3)]. There are many examples of non-concerted epoxidations ranging from those that show almost complete retention of configuration such as that brought about by alkynes and ozone [17] to those that show extensive loss of stereochemistry, namely those with peroxyacetyl radicals in the gas phase [21] or with $Fe^{III}(acac)_3$ and hydrogen peroxide in acetonitrile.[30]



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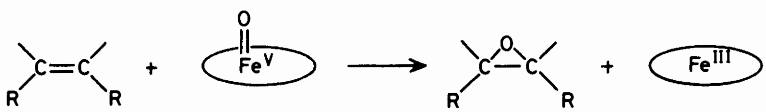

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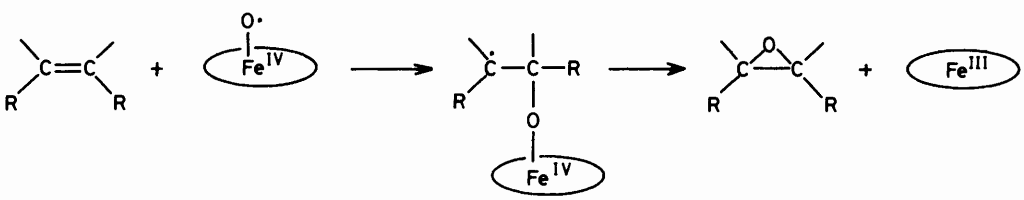
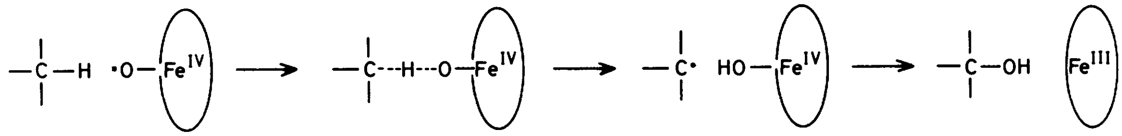


(3)

(2)

Some of the data from the oxidation of saturated C–H bonds are inconsistent with a concerted insertion mechanism for this process. Groves [6] has reported that the hydroxylation of *cis*-decalin is not totally stereospecific and gives *cis*- and *trans*-9-decalols in a 5 : 1 ratio respectively and the allylic hydroxylation of 1,2-dideuteriocyclohexene results in a partial allylic rearrangement.[33] We have observed a large kinetic isotope effect for the demethylation of anisole and [Me-$^2H_3$]anisole.[4] These results are more consistent with C–H bond cleavage involving hydrogen atom abstraction by an oxy-radical with a linear C–H–O transition state [reaction (4)] than insertion into the C–H bond by a singlet oxenoid species which by analogy with the reactions of singlet carbenes and nitrenes [34] is generally thought to proceed *via* a triangular transition state [reaction (5)]. In this respect it is noteworthy that some recent calculations by Pudzianowski and Loew [35] suggest that singlet oxygen [$O(^1S)$] (a model for a singlet oxenoid species) may react with methane by abstraction *via* an almost linear transition state followed by rearrangement rather than by a direct



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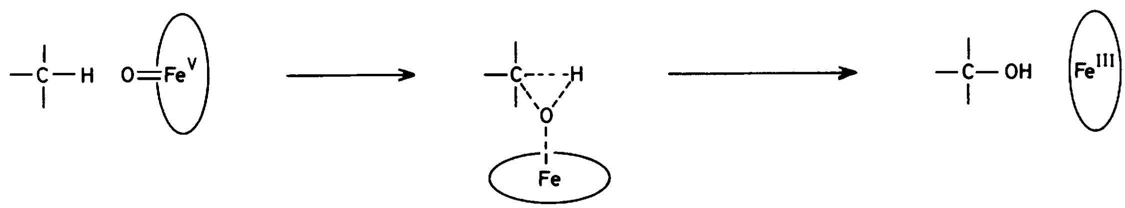

(5)

concerted insertion. Such a mechanism for C–H oxidation might not be totally stereospecific and might involve a large kinetic isotope effect.

Work is in progress to distinguish between the alternative mechanisms for oxidation by the model system.

EXPERIMENTAL

Materials.—All the materials were commercial reagent grade unless otherwise stated and were obtained from Aldrich Chemical Co. Ltd., Fisons Scientific Apparatus Ltd., or Koch-Light Ltd. The nitrogen gas was British Oxygen white spot grade. Deuterium gas was from Matheson.

The alkenes, with the exception of 4-nitrostyrene, and aromatic compounds were commerically available and purified either by distillation or recrystallisation before use. 4-Nitrostyrene was prepared by dehydrobromination of 4-nitrophenethyl bromide [36] following Strassburg *et al.*[37] The stereochemical purities of *cis-* and *trans*-4-methylpent-2-ene (g.c. analysis [38]) were 99.8 and >99.9% respectively and of *cis-* and *trans*-stilbene (h.p.l.c. analysis) 95.1 and 99.9%, respectively. [4-^{2}H]Anisole (84.7% $^2H_1$) and [1,4-$^2H_2$]naphthalene (95.5% $^2H_2$, 4.5% $^2H_1$) were prepared and analysed as previously described.[39] The extent of random labelling in the naphthalene was <0.5% (^{13}C and ^{2}H n.m.r.).

The epoxides of the aliphatic alkenes, styrene, 4-methylstyrene, and 4-chlorostyrene were prepared from the alkenes with peracetic acid or 3-chloroperbenzoic acid by standard procedures [24] and purified by distillation or preparative g.c. The epoxides of 4-methoxy- and 3-chloro-styrene were prepared from the corresponding substituted benzaldehyde by the method of Kutsuma *et al.*[40] 4-Nitrostyrene epoxide was prepared from 4-nitrostyrene following Westkaemper and Hanzlik.[41] *cis*-Stilbene epoxide was prepared using the method of Imuta and Ziffer.[42] Phenanthrene 9,10-epoxide and acenaphthylene 1,2-epoxide were prepared by oxidation of the parent hydrocarbon following Krishnan *et al.*[26b] The physical properties and spectral data of the epoxides synthesised in this study are recorded in Tables 7—9.

[2,4-$^2H_2$]-1-Naphthol (both 2- and 4-positions 79 ± 2% deuteriated, ^{1}H n.m.r.) was prepared from 1-naphthol by exchange in acidified [$^2H_4$]methanol. [2,4-$^2H_2$]-1-Naphthol trimethylsilyl ether was obtained from the deuterionaphthol by reaction with bis(trimethylsilyl)acetamide and shown to contain $^2H_2$, 68.5; $^2H_1$, 27.9; and $^2H_0$, 3.7% (g.c.–m.s.). The good agreement between the measurement of the deuterium content of the 1-naphthol by ^{1}H n.m.r. with that of the silyl ether by g.c.–m.s. indicates that there is no loss of deuterium during silylation.

meso-*Tetrakis(pentafluorophenyl)porphyrin* was prepared by the method of Alder *et al.*[50] and had δ_H ($CDCl_3$) 8.87 (s);

TABLE 7

Physical properties and ^{1}H n.m.r. data of epoxides of aliphatic alkenes

Epoxide	B.p. (°C)	^{1}H n.m.r. data (δ) Epoxy H	Alkyl substituent
2,3-Epoxy-2,3-dimethylbutane	90—93 (lit.,[43] 90.5—91)		1.32 (12 H, s)
2,3-Epoxy-2-methylbutane	72—75 (lit.,[43] 76—76.5)	2.80 (1 H, q)	1.27 (6 H, s) 1.23 (3 H, d)
1,2-Epoxy-1-methylcyclohexane	136—137 (lit.,[44] 137—138)	2.90 (1 H, t)	1.25 (3 H, s) 2.15—1.00 (8 H, m)
cis-2,3-Epoxy-4-methylpentane	94—97 (lit.,[45] 99—100)	3.01 (1 H, dq) 2.51 (1 H, dd)	1.41 (1 H, m) 1.26 (3 H, d) 1.12 (3 H, d) 0.94 (3 H, d)
trans-2,3-Epoxy-4-methylpentane	94—95 (lit.,[46] 96—97)	2.79 (1 H, dq) 2.40 (1 H, dd)	1.50 (1 H, m) 1.29 (3 H, d) 1.00 (3 H, d) 0.92 (3 H, d)
1,2-Epoxyoctane	162—167 (lit.,[44] 86—87 at 47 mmHg)	3.05—2.31 (3 H, m)	1.70—0.30 (13 H, m)

δ_F ($CDCl_3$) relative to $CFCl_3$ −136.97 (2 F, m, Ar−F_{ortho}), −151.80 (1 F, m, Ar−F_{para}), and −161.88 p.p.m. (2 F, m, Ar−F_{meta}) (Found: C, 54.15; H, 1.4; N, 6.05. $C_{44}H_{10}F_{20}N_4$ requires C, 54.25; H, 1.05; N, 5.75%); $\lambda_{max.}$ (CH_2Cl_2) 413 (log ε 4.33), 507 (3.17), 586 (2.77), and 6.59 nm (2.46).

Tetraphenylporphinatoiron(III) chloride and *tetrakis-(pentafluorophenyl)porphinatoiron*(III) *chloride* were prepared following the method of Rothemund and Menotti [51] (the latter compound, Found: C, 49.7; H, 1.2; N 5.35. $C_{44}H_8ClF_{20}N_4Fe$ requires C, 49.7; H, 0.75; N, 5.3%), $\lambda_{max.}$ (CH_2Cl_2) 349 (log ε 3.75), 412 (4.06), 632 (2.74), and 505 nm (3.08).

Iodosylbenzene was prepared following Lucas *et al.*[52]

Methods.—Glass columns were used in a Pye-Unicam 204 gas chromatograph with a flame ionisation detector for g.c. analyses. The following packing materials were used for the oxidation products from: the aliphatic alkenes, 20% w/w SE30 on Celite AW (80—120 mesh); the styrenes, anisole, and toluene, 2, 5, or 10% w/w diethylene glycol adipate polyester (LAC 2R 446 Cambridge Industries Inc.) on Celite AW (80—120 mesh); and naphthalene, 1% w/w OV 225 on Gas Chrom Q (100—120 mesh). For combined g.c.–mass spectrometry a Pye 104 gas chromatograph was coupled to an AEI MS 30 spectrometer. Reverse-phase h.p.l.c. with water–methanol eluent was used to analyse the products from the stilbenes, phenanthrene, acenaphthylene, and pyrene. Analytical h.p.l.c. was carried out with a Du Pont 830 chromatograph, using stainless steel columns (25 × 0.4 cm) packed with Partisil-10 ODS 2 (Whatman), coupled to a Du Pont 837 variable wavelength u.v. detector. Preparative h.p.l.c. used the same instrument with a stainless steel (50 × 0.94 cm) column packed with Partisil-10 ODS-3 (Whatman).

^1H N.m.r. spectra were recorded on JEOL JNM-MH-100 (100 MHz) and Varian EM 360A (60 MHz) spectrometers except for that of pyrene 4,5-epoxide (obtained from the oxidation of pyrene) which was measured with a Bruker WH 400 (400 MHz) spectrometer. ^{13}C and ^2H n.m.r. spectra were recorded on a JEOL FX 90Q spectrometer.

Oxidation Procedure.—Iodosylbenzene (0.45 mmol) was added to a stirred solution of Fe^{III}TPPCl (4.2 × 10^{-2} mmol) and substrate (5 mmol) in dichloromethane (5 cm^3) under nitrogen or in air. After 30 min at room temperature, when all the iodosylbenzene had been consumed, the mixture was analysed by chromatography. For the reactions of the polycyclic hydrocarbons the product mixture was concentrated before analysis.

For benzene and toluene the following procedure was used. Iodosylbenzene (1.36 mmol) was added to a stirred solution of Fe^{III}TPPCl (4.2 × 10^{-2} mmol) and aromatic substrate (10 mmol) in dichloromethane (3 cm^3). After 30 min more Fe^{III}TPPCl (4.2 × 10^{-2} mmol) was added and the mixture was analysed after 1 h.

The deuterium content of the 4-methoxyphenol from [4-^{2}H]anisole was obtained by g.c.–m.s. analysis of the reaction product. The 1-naphthol from [1,4-$^2H_2$]naphthalene was converted into its trimethylsilyl ether prior to g.c.–m.s. analysis.

Competition Experiments.—The competition experiments were carried out as described above at room temperature with 5 mmol of each substrate. The low temperature competition experiment between cyclohexene and 1-methylcyclohexene used the same method except that the reaction was maintained at —10 °C and the mixture was monitored after 1, 8, 16, and 24 min and at completion after 45 min.

TABLE 8

Physical properties and ^1H n.m.r. spectral data of styrene epoxides

Epoxide	B.p. or m.p. (°C)	^1H n.m.r. data (δ) Aromatic	Epoxy H	Substituent
Styrene epoxide	b.p. 76 at 5 mmHg (lit.,[47] 71 at 11 mmHg)	7.15 (5 H, s)	3.60, 2.83, 2.53	
4-Methylstyrene epoxide	b.p. 44 at 0.3 mmHg (lit.,[48] 57 at 1.5 mmHg)	7.15 (4 H, s)	3.75, 3.05, 2.70	2.30 (3 H, s)
4-Methoxystyrene epoxide	m.p. 19—23 (lit.,[49] 18—22)	6.70 (2 H, d) 7.15 (2 H, d)	3.75, 3.05, 2.75	3.75 (3 H, s)
3-Chlorostyrene epoxide	b.p. 76 at 16 mmHg (lit.,[48] 90 at 8.5 mmHg)	7.15 (4 H, m)	3.75, 3.05, 2.68	
4-Chlorostyrene epoxide	b.p. 35 at 0.1 mmHg (lit.,[48] 37—38 at 0.1 mmHg)	7.20 (4 H, m)	3.75, 3.08, 2.70	
4-Nitrostyrene epoxide	m.p. 84—85 (lit.,[48] 84—85)	7.40 (2 H, d) 8.15 (2 H, d)	3.95, 3.20, 2.80	

TABLE 9

Physical properties and spectral data of epoxides of *cis*-stilbene, phenanthrene, and acenaphthylene

Epoxide	M.p. (°C)	Mass spectrum $M^{+\cdot}$	^1H n.m.r. data (δ)
cis-Stilbene epoxide	37—38 (lit.,[24] 37—37.5)		7.2 (10 H, s) and 4.3 (2 H, s)
Phenanthrene 9,10-epoxide	124—126 (lit.,[32] 124—125)	194	8.1—7.2 (8 H, m) and 4.5 (2 H, s)
Acenaphthylene 1,2-epoxide	82—83 (lit.,[42] 83—84)	168	7.8—7.4 (6 H, m) and 4.9 (2 H, s)

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