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PAPER

Chemoselective epoxidation of electron rich and electron deficient olefins catalyzed by *meso*-tetraarylporphyrin iron(III) chlorides in imidazolium ionic liquids†

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The oxygenation of substrates containing both electron rich and electron deficient olefins (**1a–b**) catalyzed by 5,10,15,20-tetraarylporphyrinatoiron(III) chlorides [TAPFe(III)Cl] with H_2O_2 gave epoxides at both electron rich and deficient olefin (**2a–b**, **3a–b**), while with iodosyl benzene (PhIO) gave the epoxides only at electron rich olefin (**3a–b**) in imidazolium ionic liquids (ILs). Further reaction of **2a–b** with sodium hydroxide in methanol gave **4a–b** by base catalysed rearrangement of enedione epoxides. Similar reaction of **4a–b** with H_2O_2 or PhIO gave the major epoxides of electron deficient olefins and electron rich olefins. The ferric peroxy anions (TAP-Fe^{III}–OO^-) are effective intermediates in the epoxidation of electron deficient olefins, whereas the high valent oxoferrylporphyrin π-cation radicals (TAP-Fe^{IV}=$O^{\bullet +}$) are involved in the epoxidation of electron rich olefins. The ILs provide the special microenvironments by the interactions of cations and anions, in which the generation of the active intermediates from TAPFe(III)Cl/[Bmim][PF_6] and monooxygen donors could be accelerated significantly.

Introduction

Cytochrome P450 is a group of heme-containing monooxygenases that play important roles in the metabolism of many physiological substrates and xenobiotics. The cytochrome P450 systems catalyze the hydroxylation of hydrocarbon, epoxidation of double bonds, oxidation of heteroatoms and dehydrogenation of substrates.[1,2] The oxygenation of a broad range of substrates, particularly by the mammalian P450s, is a feature indicative of both an active site that can accommodate a wide variety of chemical moieties, and the production of potent oxidants, electrophilic and nucleophilic in nature, which serve as effective and often indiscriminant catalysts.[3] The selective substrate gives one or more products by the reaction of different reactive intermediates of cytochrome P450 enzyme system.[4] The reactions of 5,10,15,20-tetraarylporphyrinatoiron(III) chlorides and mono oxygen donors mimics the different reactions of cytochrome P450 and related mono hemeoxygenases in different reaction conditions.[5,6] The *meso* substituents and axial ligands of metalloporphyrins influence the oxidative potential of the reactive intermediates formed by the reaction of mono oxygen donors with TAPFe(III)Cl in different reaction conditions.[7,8]

Solvents constitute a major factor in deciding the efficacy of an environmentally friendly technology to develop new products and processes.[9] Room-temperature ionic liquids (RTILs) are potentially environmentally benign solvents for various organic and biochemical transformations.[9–17] The hydrophilicity, hydrophobicity, Lewis acidity, viscosity and density of the ILs can be changed by the choice of organic cation, inorganic anion, and the length of the alkyl chain attached to the ILs.[9–17] The ILs have been used in organocatalysis along with Lewis acids, Lewis bases, Brønsted acids and Brønsted bases.[9–17] The reactions of cytochrome P450 in ILs have been studied in recent years.[18–20] Metalloporphyrinoids have been used as catalysts to mimic the various reactions of heme enzymes and proteins in imidazolium ILs.[9] In order to understand the role of *meso* substituents, reaction media and oxidants on the epoxidation of electron rich and electron deficient olefins, we have examined the epoxidation of substrates containing both the electron rich and electron deficient olefins within a single molecule, with different monooxygen donors catalyzed by 5,10,15,20-tetraaryliron(III) porphyrins in imidazolium ILs.

Results and discussion

The reaction of 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (**1a**, 1 mmol) with H_2O_2 catalyzed by (*p*-OMe)$_4$TAPFe(III)Cl (**7a**) in [Bmim][PF_6] at room temperature gave two major products, 1a,2a,3,6,6a,7a-hexahydro-3,6-methanonaphth[2,3-b]oxirene-2,7-dione (**2a**) and 1a,2,2a,6a,7,7a-hexahydro-2,7-methanonaphth-[2,3-b]oxirene-3,6-dione (**3a**) in 76.2% and 12.3% yields respectively

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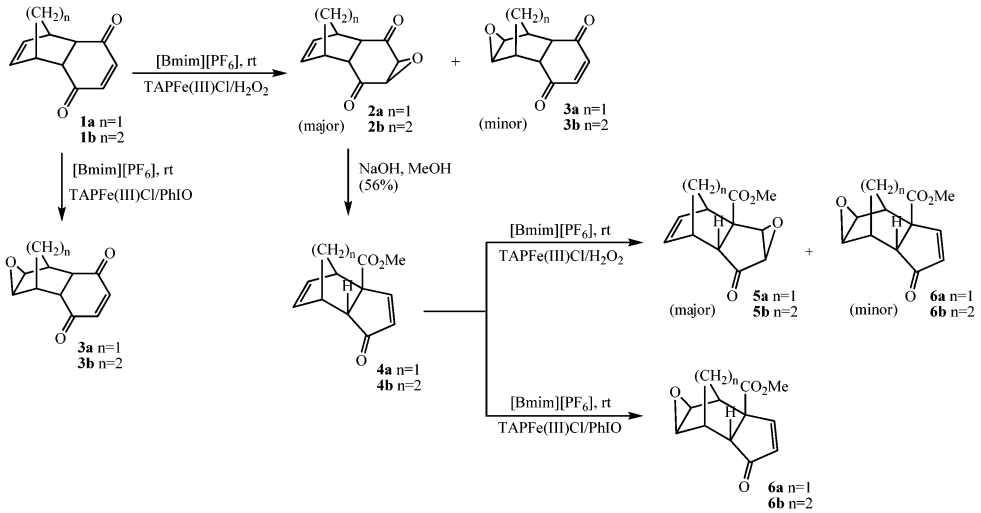
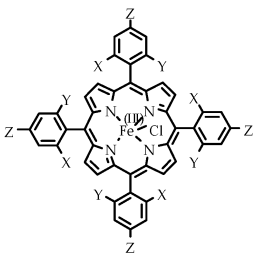


Scheme 1 The oxidation of adducts with H_2O_2 and PhIO catalyzed by TAPFe(III)Cl in IL.



7a X=Y=H, Z=OMe
7b X=Y=Z=H
7c X=Y=Cl, Z= H

Fig. 1 Different aryl substituted *meso*-tetraarylporphyrin iron(III) chlorides used as catalysts in the reaction.

(Scheme 1, Fig. 1, Table 1), while in the absence of catalyst, **1a** did not gave any product even after stirring the reaction mixture for 24 h in [Bmim][PF_6] ILs.

The reaction of **1a** with H_2O_2 catalyzed by Cl_8TAPFe(III)Cl (**7c**) in [Bmim][PF_6] gave **2a** and **3a** in 59.7% and 21.3% yields respectively (Table 2). The reaction of **1a** in the presence of **7a–c** proceeds much faster and more efficiently in different ILs such as [Bmim][Br], [Bmim][BF_4], [Bmim][PF_6] and [Bmim][OAc], compared to organic solvents (Table 1). However, the reaction of **1a** with PhIO catalyzed by **7a** gave exclusively **3a** in 64.9% in [Bmim][PF_6] IL. The yield of **2a** was improved substantially using catalysts bearing electron-donating groups on the phenyl ring (**7a**), while with electron-withdrawing groups (**7c**) the yield of **3a** was increased indicating the stabilization of the different intermediates by different iron(III) porphyrins (Table 2). The stability and the recyclability of the TAPFe(III)Cl/[Bmim][PF_6] catalytic system was examined by repetitive use of the catalyst and ILs. There is no significant decrease in reactivity and selectivity of catalyst up to five cycles in the epoxidation of **1a** in ILs.

The reaction of **1b** with H_2O_2 catalysed by **7a** in [Bmim][PF_6] gave **2b** and **3b** in 78.6% and 14.8% yields while with **7c** as catalyst **2b** and **3b** were obtained in 57.8% and 25.5% yields respectively (Table 2). The reaction of **1b** with PhIO catalysed by **7a** in [Bmim][PF_6] gave exclusively **3b** in

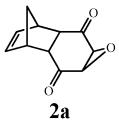
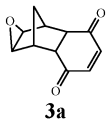
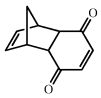
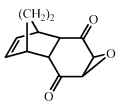
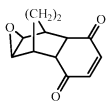
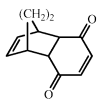
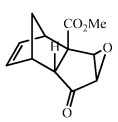
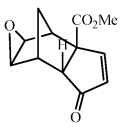
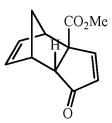
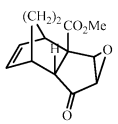
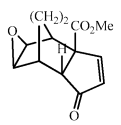
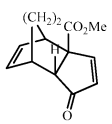
Table 1 Effect of solvent on the epoxidation of **1a** using different mono-oxygen donors catalyzed by (*p*-OMe)$_4$TAPFe(III)Cl (**7a**)

		% Yield[a] of epoxides	
System[b]	Time (h)	**2a**	**3a**
ACN/H_2O_2	3.0	46.8	4.1
DCM/H_2O_2	3.0	38.1	3.7
DCM : [Bmim][PF_6] (9 : 1)/H_2O_2	3.0	44.4	5.3
DCM : [Bmim][PF_6] (3 : 7)/H_2O_2	3.0	75.4	11.8
[Bmim][Br]/H_2O_2	3.0	60.7	24.9
[Bmim][BF_4]/H_2O_2	3.0	71.6	16.2
[Bmim][PF_6]/H_2O_2	3.0	76.2	12.3
[Bmim][OAc]/H_2O_2	3.0	86.5	4.4
DCM-[Bu_4N][Br](3 : 7)/H_2O_2	3.0	39.4	—
DCM-([$CH_3(CH_2)_{15}(CH_3)_3N$]Br) (3 : 7)/H_2O_2	3.0	42.7	—
ACN/PhIO	3.0	—	27.8
DCM/PhIO	3.0	—	38.8
[Bmim][Br]/PhIO	3.0	—	76.3
[Bmim][BF_4]/PhIO	3.0	—	73.7
[Bmim][PF_6]/PhIO	3.0	—	64.9
[Bmim][OAc]/PhIO	3.0	—	43.2

[a] HPLC yields (C-18 reverse phase column); water : MeOH : acetonitrile = 60 : 35 : 5, flow rate = 0.5 mL min^{-1}, monitored at 290 nm). [b] Substrate : oxidant : catalyst = 100 : 200 : 1 in 1 mL IL; ACN = Acetonitrile; DCM = dichloromethane; [Bmim][BF_4] = butylmethylimidazolium bromide; [Bmim][BF_4] = butylmethylimidazolium tetraboroflourate; [Bmim][PF_6] = butylmethyl imidazolium hexaflourophospahte; [Bmim][OAc] = butylmethylimidazolium acetate.

66.7% yields while with **7c** as catalyst **3b** was obtained in 77.2% yields respectively (Table 2). The reaction of **2a–b** with sodium hydroxide in methanol gave **4a–b** in moderate yields. The formation of **4a–b** from **2a–b** may be explained by base catalysed rearrangement of enedione epoxide (**2a–b**) in sodium hydroxide in methanol.[21] The oxidation of **1c** with H_2O_2 as monooxygen donor catalyzed by in [Bmim][PF_6] gave **5a** and **6a** in 62.8% and 5.3% yields while with **7c** as catalyst **5a** and **6a** were obtained in 46.4% and 17.2% yields respectively (Table 2). The reaction of **4b** with PhIO as monooxygen donor

Table 2 Epoxidation of different alkenes (**1a–b**, **4a–b**) using H_2O_2 or PhIO catalyzed by different TAPFe(III)Cl (**7a–c**) in [Bmim][PF_6]

Substrate	System[a]	Time (h)	% Yield[b] of epoxides	
			 **2a**	 **3a**
 **1a**	**7a**/H_2O_2	3.0	76.2	12.3
	7b/H_2O_2	3.0	64.4	16.6
	7c/H_2O_2	3.0	59.7	21.3
	7a/PhIO	3.0	—	64.9
	7b/PhIO	3.0	—	70.7
	7c/PhIO	3.0	—	76.6
			 **2b**	 **3b**
 **1b**	**7a**/H_2O_2	3.0	78.6	14.8
	7b/H_2O_2	3.0	67.4	18.7
	7c/H_2O_2	3.0	57.8	25.5
	7a/PhIO	3.0	—	66.7
	7b/PhIO	3.0	—	71.3
	7c/PhIO	3.0	—	77.2
			 **5a**	 **6a**
 **4a**	**7a**/H_2O_2	3.0	62.8	5.3
	7b/H_2O_2	3.0	58.2	10.5
	7c/H_2O_2	3.0	46.4	17.2
	7a/PhIO	3.0	—	52.4
	7b/PhIO	3.0	—	57.6
	7c/PhIO	3.0	—	68.7
			 **5b**	 **6b**
 **4b**	**7a**/H_2O_2	3.0	64.5	7.1
	7b/H_2O_2	3.0	61.3	12.6
	7c/H_2O_2	3.0	47.6	19.4
	7a/PhIO	3.0	—	55.5
	7b/PhIO	3.0	—	59.4
	7c/PhIO	3.0	—	70.6

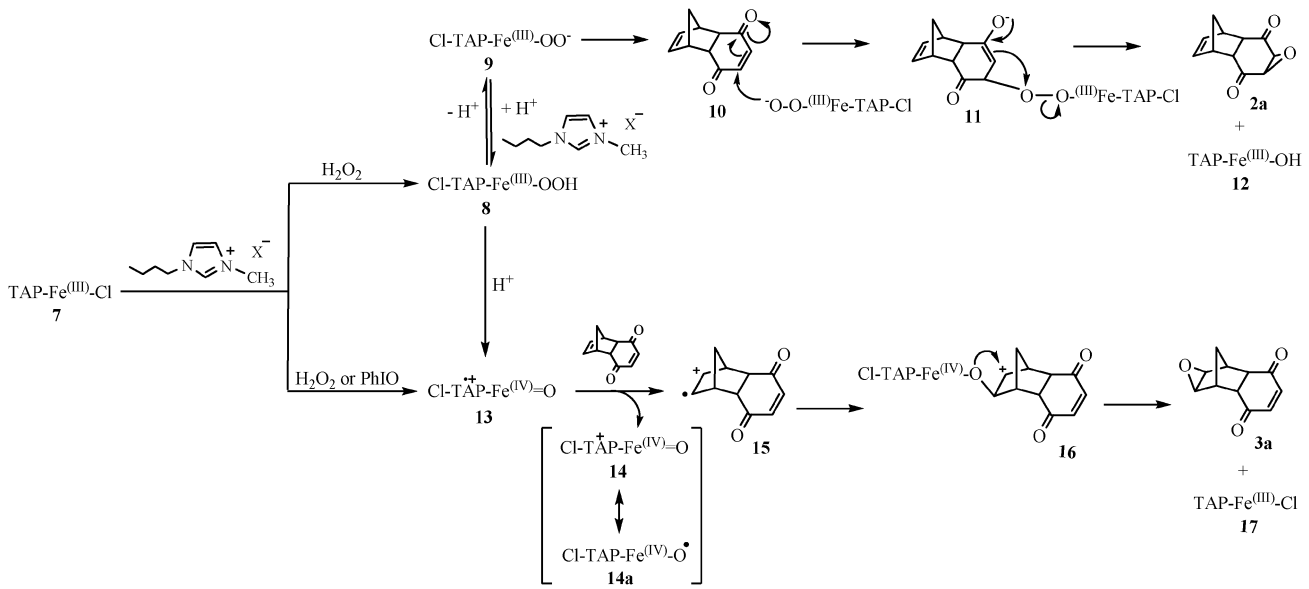
[a] Substrate/monooxygen donor/catalyst = 100 : 200 : 1 in 1 ml IL. [b] HPLC yields.

catalysed by **7a** in [Bmim][PF_6] gave exclusively **6b** in 52.4% yields, while with **7c** as catalyst **6b** was obtained in 68.7% yields respectively (Table 2). The reaction of **4b** with H_2O_2 catalyzed by **7a** in [Bmim][PF_6] gave **5b** and **6b** in 64.5% and 7.1% yields and with **7c** as catalyst **5b** and **6b** were obtained in 47.6% and 19.4% yields respectively (Table 2). The reaction of **4b** with PhIO catalysed by **7a** in [Bmim][PF_6] gave **6b** in 55.5% yields while with **7c** as catalyst **6b** was obtained in 70.6% yields respectively (Table 2).

In order to understand the effect of ILs, a mixed solvent of [Bmim][PF_6] and DCM was used in the epoxidation of **1a**. Epoxidation reaction was slow in DCM whereas when [Bmim][PF_6] was added to DCM to form a homogeneous solution, the catalytic activity was markedly enhanced. The reaction catalysed by **7c** using H_2O_2 as oxygen donor, 44.4% of **2a** and 5.3% of **3a** were obtained after addition of 10% of IL in DCM (Table 1, entry 3). The increasing percentage of ILs also increased the yields of the products. When 70% of the ILs were added to DCM, the yield of epoxide tended to remain constant (Table 1, entry 4). This was also supported by the changes in the UV-Visible spectra of TAPFe(III)Cl with increasing concentration of ILs in dichloromethane. A decrease in the absorption at 506 and 652 nm and a simultaneous increase in the absorption at 547 nm (Fig. 1S, ESI†), with isosbestic points at 495, 525 and 590 nm in the UV-Visible spectra of TAPFe(III)Cl in dichloromethane has been observed. The results were similar to that are reported with *N*-methyl imidazole.[7,22] The epoxidation of **1a** with H_2O_2 catalyzed by **7c** gave 86.5% of **2a** in [Bmim][OAc] (Table 1, entry 8), whereas in the absence of **7c** 6.4% of **2a** was obtained in [Bmim][OAc]. The significant increase in the yields of the **2a** may be explained by catalysis with iron porhyrin and organocatalysis by imidazolium acetate. The ionic liquid [Bmim][Br] with $[Br]^-$ as counter ion comparatively gave lower yields of **2a** and higher yields of **3a** epoxides (Table 1, entry 5). Different types of organic tetraalkylammonium ion salts were also used to determine the effect of the ions. Neither the short-chain tetrabutylammonium bromide ($[Bu_4N]Br$) nor the long-chain cetyltrimethyl ammonium bromide ($[CH_3(CH_2)_{15}(CH_3)_3N]Br$) exhibited much acceleration on the epoxidation (Table 1, entry 9–10). The above results indicate that the anion, in addition to the cation of the ionic liquid, presents an important role on the activity of catalyst and it is evident that the ILs can provide a special microenvironment for the formation of the active species in the reaction.[15–17,20]

In metalloporphyrin catalyzed oxidation reactions, similar to cytochrome P450 catalyzed metabolic reactions in biological systems, various electrophilic and nucleophilic catalytic intermediate species such as a ferric hydroperoxy complex (Fe^{III}–OOH, **8**), ferric peroxy anions (Fe^{III}–OO^-, **9**) and oxoferrylporphyrin π-cation radicals (Fe^{IV}=$O^{\bullet+}$, **13**), have been postulated (Scheme 2).[3,23,24]

The high yields of the different epoxides in ILs can be attributed to the stabilization of the highly charged iron-peroxo or oxo intermediates (compound I of cytochrome P450) generated during the reaction.[15–20] The formation of the epoxide (**2a**) at the electron deficient olefin can be attributed to the formation of ferric peroxo complexes (**9**).[25–27] The reaction of H_2O_2 and TAPFe(III)Cl forms **8** which equilibrate to **9**, depending on the substituents on the phenyl ring of porphyrins as well as axial ligands (Scheme 2).[28–30] The formation of **9** was confirmed by the appearance of a Soret band at 432 nm and Q bands at 548 and 664 nm in the UV-Visible spectra.[25,26] This was further confirmed when the reaction was monitored by ESR spectroscopy. The signals at $g = 4.5$ and $g = 9.3$ was observed for the Fe(III)OO^- (**9**) complexes,[31] which disappeared on addition of the substrate (**1a**) (Fig. 8S(a) ESI†). The lower yields of **2a** with **7c** can be attributed to the reduced nucleophilic character of oxygen atom in iron(III)peroxo complexes due to the presence of strong electron withdrawing chlorine substituents on the porphyrin ring.[32]



Scheme 2 Mechanism proposed for the epoxidation of electron rich and deficient olefins in ILs.

The high yields of **2a** with porphyrins bearing an electron donating group can be attributed to the generation of more nucleophilic and reactive intermediate (**9**) during the reaction. This type of nucleophilic oxygen atom transfer mimics the direct nucleophilic attack on the enzyme bound substrate proposed for certain types of P450 enzymes.[28] The high yields of the epoxide (**2a**) in basic ILs (Table 1, entries 8), can be attributed to the assistance provided by the anion in the generation of **9** by non-covalent interactions of imdazolium ILs.[9,33,34]

In the reaction of **1a** with PhIO catalysed by metalloporphyrin (**7c**), the formation of epoxide **3a** may be explained by the formation of high valent-oxo-iron(IV) radical cation (**13**) from PhIO or H_2O_2 as monooxygen donors (Scheme 2).[35] The intermediate **13**, abstracts an electron to **1a** to generate the olefin cation radical (**15**), the recombination of **14a** with **15** forms the intermediate **16**, which leads to **3a** (Scheme 2). This was supported by the presence of a low intensity ESR signal at $g = 3.85$ characteristic of **13** which disappeared in the presence of **1a** (Fig. 8S(b) ESI†).[35,36] The high yields of **3a** with catalysts bearing electron-withdrawing groups (**7c**) could be attributed to the generation of the more electrophilic and reactive intermediate (**13**) in the reaction, which showed greater selectivity towards electron rich olefin in **1a**.

Conclusions

In conclusion, the oxygenation of substrates containing both electron rich and electron deficient olefins within a single molecule, with H_2O_2 gave the epoxide at electron deficient olefin as major product along with the epoxide at electron rich olefin as minor product. The epoxidation with PhIO catalyzed by TAPFe(III)Cl, at the electron rich olefin has been observed in different imidazolium ILs. Porphyrins bearing electron-withdrawing substituents on the phenyl ring favour the epoxidation at electron rich olefins, while porphyrins bearing electron-donating substituents on the phenyl ring favour the epoxidation at electron deficient olefins. The ionic liquid provides a special microenvironment by the interactions of cations and anions, in which the generation of the active intermediates from TAPFe(III)Cl/[Bmim][PF_6] and monooxygen donor could be accelerated significantly.

Experimental

Synthesis of the starting materials

The required iron porphyrins were prepared and purified by modification of reported procedures.[30,37] Most of the imidazolium ILs were prepared and purified by minor modifications of known procedures.[10,38]

1,4,4a,8a-Tetrahydro-1,4-methanonaphthalene-5,8-dione (1a)

The reaction of *p*-benzoquinone with cyclopentadiene was carried out by the slight modification of the reported method.[39] *p*-Benzoquinone (0.1 mmol) was dissolved in [Bmim][PF_6] and the freshly cracked cyclopentadiene was added dropwise to it over a period of 45 min with stirring at room temperature. After completion, the reaction mixture was extracted with EtOAc. The organic layer was separated, dried over anhy. Na_2SO_4 and evaporated under reduced pressure to afford the pale yellow crystals.

IR (KBr, cm^{-1}): 2424, 1668, 1603, 1442, 1385, 1280, 1055, 1044, 865, 735; ^1H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.55 (br s, 2H), 3.20 (s, 2H), 3.52 (s, 2H), 6.01 (s, 2H), 6.5 (s, 2H); ESI-MS: 175.1241 (M + 1).

1,4,4a,8a-Tetrahydro-1,4-ethanonaphthalene-5,8-dione (1b)

The reaction of *p*-benzoquinone with cyclohexa-1,3-diene was carried out by the slight modification of the reported method.[40] A mixture of cyclohexa-1,3-diene (0.1 mmol) and *p*-benzoquinone (0.1 mmol) were stirred in [Bmim][PF_6] at 60–70 °C. The completion of reaction was monitored by TLC. After completion, the reaction mixture was extracted with EtOAc. The organic layer was separated, dried over anhy.

Na_2SO_4 and evaporated under reduced pressure to afford the crude product. The crude product was recrystallized with ethanol.

IR (KBr, cm^{-1}): 2430, 1665, 1658, 1442, 1382, 1246, 1191, 1044; ^1H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.48 (br s, 4 H), 2.92 (s, 2H), 3.20 (s, 2H), 6.15 (s, 2H), 6.57 (s, 2H); ESI-MS: 189.1324 (M + 1).

Reaction of alkenes (1a–b) with hydrogen peroxide catalyzed by TAPFe(III)Cl in different ILs

The Diels Alder adduct (**1a–b**, 1 mmol) was dissolved in [Bmim][PF_6] immobilised with 5,10,15,20-tetraarylporphyrinatoiron(III) chloride (0.01 mmol) and the reaction mixture was stirred at room temperature. To the reaction mixture H_2O_2 (2 mmol) was added in small interval of time. The completion of the reaction was monitored by TLC, after completion, the reaction mixture was extracted with ethyl acetate. The organic layer was separated, dried over anhy. Na_2SO_4 and evaporated under reduced pressure and purified by column chromatography to afford the corresponding epoxides.

1a,2a,3,6,6a,7a-Hexahydro-3,6-methanonaphth[2,3-b]oxirene-2,7-dione (2a)

IR (KBr, cm^{-1}): 2967, 1716, 1457, 1341, 1309, 1260, 1191, 1004, 847, 735, 640; ^1H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.3 (s, 2H), 2.8 (d, 2H, J = 9.8 Hz), 3.22 (s, 2H), 3.54 (s, 2H), 3.57 (d, 2H, J = 7.7 Hz), 5.98 (s, 2H); ESI-MS: 191.0871(M + 1).

1a,2a,3,6,6a,7a-Hexahydro-3,6-ethanonaphth[2,3-b]oxirene-2,7-dione (2b)

IR (KBr, cm^{-1}): 2954, 1718, 1600, 1309, 1262, 1195, 1006, 850, 738, 634; ^1H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.5 (d, 2H, J = 9.4 Hz), 1.7 (d, 2H, J = 10.1 Hz), 2.1 (s, 2H), 2.8 (s, 2H), 3.2 (s, 2H), 3.7 (s, 2H); ESI-MS: 205.0864 (M + 1).

Synthesis of alkenes (4a–b)

The alkenes (**4a–b**) were synthesized by a slight modification of the reported method.[41] A saturated solution of sodium hydroxide in methanol was prepared by dissolving sodium hydroxide (12.5 g) in dry methanol (50 mL) and was allowed to stand at room temperature for 2 days before use. The saturated methanolic sodium hydroxide solution (1.75 mL) was added to a warm solution of (**2a–b**, 26.3 mmol) in methanol (100 mL). The reaction mixture was stirred at 45 °C for 1 h. The resulting solution was concentrated under reduced pressure. The residue was diluted with water and then extracted with ether. The organic layer was separated, dried over anhy. Na_2SO_4, filtered, evaporated under reduced pressure and purified by column chromatography to afford the corresponding epoxides.

4,7-Methano-3aH-indene-3a-carboxylic acid, 1,4,7,7a-tetrahydro-1-oxo-, methyl ester (4a)

IR (KBr, cm^{-1}) 3050, 2966, 1707, 1692, 1435, 1226, 1030, 850, 738; ^1H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.35 (d, J = 9.2 Hz, 1H), 1.61 (d, J = 10.5 Hz, 1H), 3.05-3.56 (m, 3 H), 3.74 (s, 3 H), 5.88 (d, J = 5.5 Hz, 1 H), 5.75–6.02 (m, 2 H), 7.35 (d, J = 5.5 Hz, 1 H); ESI-MS: 205.1726 (M + 1).

4,7-Ethano-1*H*-indene-3a(4H)-carboxylic acid, 7,7a-dihydro-1-oxo-, methyl ester (4b)

IR (KBr, cm^{-1}) 3000, 2942, 1700, 1685, 1425, 1218, 1012, 832, 733; ^1H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.31(d, J = 9.8 Hz, 2H), 1.42 (d, J = 9.8 Hz, 2H), 3.1–3.44 (m, 5 H), 3.72 (s, 3 H), 5.82 (d, J = 6.0 Hz, 1 H), 5.8–6.1 (m, 2 H), 7.28 (d, J = 6.0 Hz, 1 H); ESI-MS: 219.1832 (M + 1).

Reaction of alkenes (4a–b) with hydrogen peroxide catalyzed by TAPFe(III)Cl in different ILs

The alkene (**4a–b**, 1 mmol) was dissolved in [Bmim][PF_6] immobilised with 5,10,15,20-tetraarylporphyrinatoiron(III) chloride (0.01 mmol) and the reaction mixture was stirred at room temperature. To the reaction mixture H_2O_2 (2 mmol) was added in short intervals. The completion of the reaction was monitored by TLC, after completion, the reaction mixture was extracted with ethyl acetate. The organic layer was separated, dried over anhy. Na_2SO_4, evaporated under reduced pressure and purified by column chromatography to afford the corresponding epoxides.

2,6-Methano-2aH-indeno[5,6-b]oxirene-2a-carboxylic acid, 1a,2,5,5a,6,6a-hexahydro-5- oxo-, methyl ester (5a)

IR (KBr, cm^{-1}): 2960, 1684, 1436, 1253, 1231, 1035, 844; ^1H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.33 (d, J = 10.5 Hz, 1H), 1.61 (d, J = 10.5 Hz, 1H), 2.84–3.27 (m, 5H), 3.75 (s, 3H), 6.11 (d, J = 5.7 Hz, 1H), 7.48 (d, J = 5.7 Hz, 1H); ESI-MS: 221.2013 (M + 1).

2,6-Ethano-2aH-indeno[5,6-b]oxirene-2a-carboxylic acid, 1a,2,5,5a,6,6a-hexahydro-5-oxo-, methyl ester (5b)

IR (KBr, cm^{-1}): 3000, 2952, 1698, 1680, 1415, 1210, 1012, 838, 730; ^1H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.44 (br s, 4H), 2.45–2.85 (m, 3H), 3.42 (s, 2H), 3.67 (s, 3H), 5.58 (s, 2H); ESI-MS: 235.1901 (M + 1).

Reaction of alkenes (1a–b) with iodosyl benzene catalyzed by TAPFe(III)Cl in different ILs

The alkene (**1a–b**, 1 mmol) was dissolved in [Bmim][PF_6] immobilised with 5,10,15,20-tetraarylporphyrinatoiron(III) chloride (0.01 mmol) and the reaction mixture was stirred at room temperature. To the reaction mixture PhIO (2 mmol) was added at short intervals. The completion of the reaction was monitored by TLC, after completion, the reaction mixture was extracted with ethyl acetate. The organic layer was separated, dried over anhy. Na_2SO_4 and evaporated under reduced pressure and purified by column chromatography to afford the corresponding epoxides.

1a,2,2a,6a,7,7a-Hexahydro-2,7-methanonaphth[2,3-b]oxirene-3,6-dione (3a)

IR (KBr, cm^{-1}) 2932, 1652, 1380, 1290, 1279, 1181, 843, 720; ^1H NMR ($CDCl_3$, 300 MHz, δ in ppm): 0.91 (d, J = 10.4 Hz, 1H), 1.55 (d, J = 10.4 Hz, 1H), 3.05 (m, 2H), 3.13 (s, 2H), 3.22 (m, 2H), 6.76 (s, 2H); ESI-MS: 191.0862 (M + 1).

1a,2,2a,6a,7,7a-Hexahydro-2,7-ethanonaphth[2,3-b]oxirene-3,6-dione (3b)

IR (KBr, cm^{-1}): 2921, 1665, 1605, 1300, 1232, 1201, 1021; ^1H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.38 (br s, 4H), 2.61 (s, 2H), 3.01 (s, 2H), 3.17 (s, 3H), 6.60 (s, 2H); ESI-MS: 205.0786 (M + 1).

Reaction of alkenes (4a–b) with iodosyl benzene catalyzed by TAPFe(III)Cl in different ILs

The alkene (**4a–b**, 1 mmol) was dissolved in [Bmim][PF_6] immobilised with 5,10,15,20-tetraarylporphyrinatoiron(III) chloride (0.01 mmol) and the reaction mixture was stirred at room temperature. To the reaction mixture PhIO (2 mmol) was added in small interval of time. The completion of the reaction was monitored by TLC, after completion, the reaction mixture was extracted with ethyl acetate. The organic layer was separated, dried over anhy. Na_2SO_4 and evaporated under reduced pressure and purified by column chromatography to afford the corresponding epoxides.

2,5-Methano-1bH-indeno[1,2-b]oxirene-1b-carboxylic acid, 1a,2,5,5a,6,6a-hexahydro-6-oxo-, methyl ester (6a)

IR (KBr, cm^{-1}): 2940, 1690, 1432, 1256, 1238, 1040, 850; ^1H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.37 (d, J = 9.6 Hz, 1H), 1.58 (d, J = 9.6 Hz, 1H), 2.74–3.19 (m, 5H), 3.64 (s, 3H), 5.98 (d, J = 5.9 Hz, 1H), 7.27 (d, J = 5.9 Hz, 1H); ESI-MS: 221.1954 (M + 1).

2,5-Ethano-1bH-indeno[1,2-b]oxirene-1b-carboxylic acid, 1a,2,5,5a,6,6a-hexahydro-6-oxo-, methyl ester (6b)

IR (KBr, cm^{-1}): 3050, 2970, 1693, 1682, 1420, 1220, 1018, 842; ^1H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.42 (d, J = 8.8 Hz, 2H), 1.76 (d, J = 8.8 Hz, 2H), 3.01–3.60 (m, 5H), 3.92 (s, 3H), 6.36 (br s, 1H), 7.73 (br s, 1H); ESI-MS: 235.2012 (M + 1).

ESR analysis

The intermediates responsible for the oxidation were prepared in an ESR sample tube by minor modification of a reported method.[42] The TAPFe(III)Cl complex (2 mM) in a [Bmim][PF_6] was placed into an ESR tube, and the solution was cooled to −80 °C in a methanol-liquid nitrogen bath. Hydrogen peroxide (2 equivalents) or PhIO (2 equivalents) was slowly added to the solution. After 2 min the solution in the ESR tube was frozen to −80 °C and was subjected to ESR measurements. An identical reaction was performed at −80 °C in the presence of substrates containing the electron rich and electron deficient olefins.

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