

Iminium Salt-Catalysed Asymmetric Epoxidation using Hydrogen Peroxide as Stoichiometric Oxidant

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Abstract: Iminium salt organocatalysts can provide high selectivity and high efficiency in catalytic asymmetric epoxidation. They are normally used in conjunction with Oxone as the stoichiometric oxidant. Oxone, however, has limited stability and is insoluble in most organic solvents; we report here for the first

time the development of a reaction system driven by hydrogen peroxide as the stoichiometric oxidant, involving an unusual double catalytic cycle.

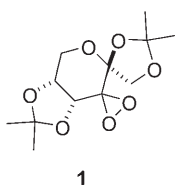
Keywords: catalysis; epoxidation; iminium salts; organocatalysis; peroxides

Introduction

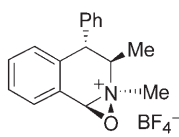
Epoxides are widely used in organic synthesis as they are highly versatile building blocks,^[1] and non-racemic chiral epoxides with high *ee* are desirable synthetic intermediates. Research over the past thirty years has seen the development of a number of methodologies capable of effecting asymmetric epoxidation.^[2] Recently, asymmetric epoxidation utilising organocatalysts has received increased attention. Shi's fructose-derived dioxirane **1**,^[3] and oxaziridinium salts such as **2**, first reported by Lusinch, have proven to be two

chiral substituent on the nitrogen atom,^[6] and a dioxane-based substituent has proved to be optimum for both yield and induction of enantioselectivity.^[7–9] Three of the most successful catalysts are the dihydroisoquinolinium salt **3a**,^[9,10] biphenylazepinium salt **4**,^[8,9,11] and binaphthalene-azepinium salt **5**, which can provide enantiomeric excesses of up to 97%.^[9,12]

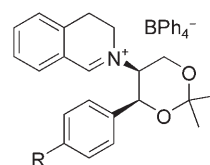
The standard iminium salt epoxidation conditions employ the triple salt Oxone (2KHSO₅·KHSO₄·K₂SO₄) as a stoichiometric oxidant, sodium carbonate, and acetonitrile:water as the solvent mixture



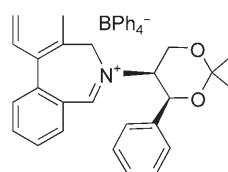
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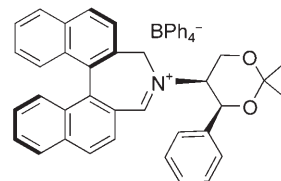
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3a, R = SO₂Me; **3b**, R = H



4

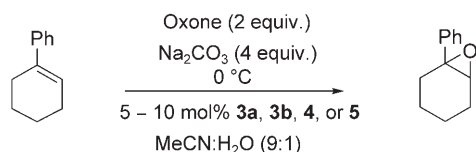


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of the most reactive types of asymmetric organocatalyst for oxygen transfer to weakly nucleophilic substrates such as unfunctionalised alkenes. Several groups have since published in the area of iminium salt-catalysed epoxidation.^[5]

We were the first to report iminium salt catalysts based on tetrahydroisoquinolines bearing an exocyclic

(Scheme 1). The presence of water is essential for Oxone solubility, and the base is essential for the epoxidation reaction to proceed. The major limitation to



Scheme 1.

these systems is the restricted range of temperatures at which the epoxidation can be performed (0 °C to room temperature). The upper limit is determined by the stability of Oxone, which decomposes relatively quickly in the basic medium at room temperature.^[13] The lower limit is determined by the use of the aqueous medium: the typical ratios of acetonitrile to water solvent used as solvent lie between 1:1 and 10:1, and the medium freezes at around –10 °C.^[7,12] A large quantity of inorganic by-product is also generated.^[2,13]

Iminium salt catalysts **3b** and **4** mediate the epoxidation of 1-phenylcyclohexene in 41% and 59% *ee* when using Oxone as the oxidant. We have recently prepared and utilised the tetraphenylphosphonium salt (TPPP) of monoperoxysulfate as a stoichiometric oxidant that is soluble in organic solvents.^[9,11] Enantiocontrol increases in these cases when using TPPP in dichloromethane solution, to 43% and 67% *ee* respectively.

We were keen to investigate other potential oxidants in order to widen the range of usable reaction conditions, but most oxidants either do not drive the catalysed reaction or generate considerable achiral product through background direct oxidation of the alkene substrates. Hydrogen peroxide is perhaps the second most environmentally friendly oxidant available after oxygen in terms of by-products, and its use as stoichiometric oxidant would allow an inexpensive and ‘green’ process to be developed.^[14] Hydrogen peroxide can oxidise electron-deficient alkenes, such as enones and conjugated esters, to their corresponding epoxides, for example in the presence of base and polyleucine catalyst.^[15]

In order to develop a hydrogen peroxide-driven system using our iminium salts as catalyst, several problems had to be addressed. Hydrogen peroxide does not induce epoxidation in the presence of iminium salts. A co-catalyst that could be oxidised to a species that is capable of oxygen transfer to an iminium salt, but would not itself induce epoxidation more rapidly than the resulting oxaziridinium salt, was therefore required. In the solid state, sodium percarbonate has been shown by X-ray crystallographic analysis to consist of a layered solid corresponding to

$\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$.^[16] Richardson and Yao have since reported that, upon addition of H_2O_2 to sodium hydrogen carbonate, an equilibrium between hydrogen carbonate and the corresponding percarbonate is established [Eq. (1)].^[17]



We reasoned that percarbonate could, in principle, oxidise an iminium salt to the corresponding oxaziridinium salt,^[18] expelling carbonate as the leaving group, the oxaziridinium salt could then directly oxidise the alkene substrate to the corresponding epoxide. We were pleased to find that commercial sodium percarbonate does indeed drive the reaction when present in large excess. The essential features of this proposed double catalytic cycle are illustrated in Scheme 2, Pathway A.

The alternative pathway B involves the hydroperoxide anion as the nucleophile that attacks the iminium salt, so generating the oxaziridinium species. In contrast to Pathway A, the inorganic promoter acts simply as a base.

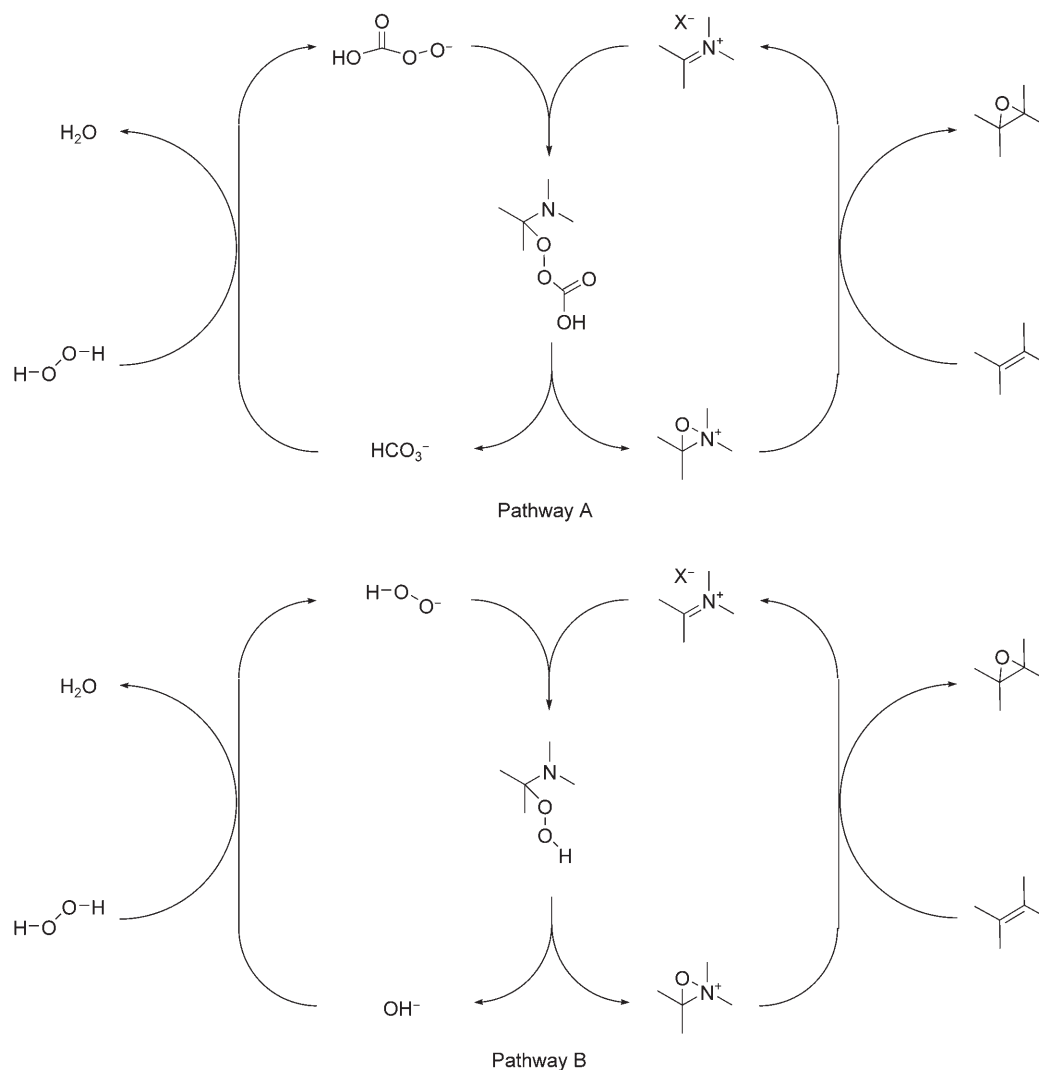
We were pleased to find that initial experiments utilising hydrogen peroxide (50% aqueous, 6 equiv.) in the presence of sodium hydrogen carbonate (0.2 equiv.) in an acetonitrile:water (9:1) solvent system using catalyst **3b** (10 mol%) induced asymmetric epoxidation of 1-phenylcyclohexene with up to 22% *ee* at 20 °C.

Results and Discussion

Effects of the Base on the Reaction

Previous work in investigating the ability of hydrogen peroxide to oxidise an iminium salt to the oxaziridinium salt in the presence of an alkene showed no evidence of epoxidation in the absence of base. In this context, we have tested several bases and other potential promoters (Table 1). Our initial reactions were completed at both 0 °C and 20 °C, using 0.2 equivalents of a range of bases, as well as potassium hydrogen phosphate, potassium hydrogen sulfate, and sodium and potassium sulfates, in addition to those salts indicated in Table 1. Based on previous work using Oxone as the stoichiometric oxidant,^[5a,o,19] we used a 9:1 ratio as the acetonitrile:water solvent system, which gives good conversion and *ee*. Catalyst **4** has shown superior reactivity to catalyst **3b**. We therefore used this solvent ratio and catalyst **4** in our investigation.

Background epoxidation utilising 0.2 equivalents of base, at 0 °C over 24 h, in the absence of any catalyst,



Scheme 2.

was not observed for sodium, potassium, or lithium carbonates, but was observed at a low level when using caesium or rubidium carbonates (<5%), and when using ammonium bicarbonate (approx 2%). At room temperature, over 24 h, the extent of the background epoxidation varied with the cation used: sodium (<5%), potassium (11%), rubidium (15%), caesium (15%) carbonates, ammonium bicarbonate (20%). These results suggest that large inorganic cations, when present, enhance background epoxidation. This may result from solubility differences and/or decreased ion association: the size of these ions may make the interionic distance sufficiently large that little electrostatic association occurs, allowing increased background reaction.

Table 1 shows that, in conjunction with catalyst **4**, the potassium salts at 0°C provide the highest enantioselectivity for reasonable conversions, giving 34% *ee* (KOH), 35% *ee* (KHCO_3), and 39% *ee* (K_2CO_3). Rubidium and caesium carbonate also gave good

enantiocontrol, but show the highest level of background epoxidation at 0°C, although this is still low at <5%. The sodium salts show decreased enantiocontrol compared with their analogous potassium salts.

It appears that the enantioselectivity achieved shows a small but significant change with the type of anion (HCO_3^- , CO_3^{2-} or OH^-) used to promote the reaction. As we have previously established, in the absence of base no epoxidation occurs, and indeed experiments containing very small amounts of base (0.01 equiv.) showed no epoxidation (entry 3). When the amount of base was increased to 0.1 equivalent, the desired epoxidation reaction furnished 1-phenylcyclohexene oxide with *ees* of 35% for NaHCO_3 , 33% for Na_2CO_3 and 28% for NaOH. We also observed that for any base added at greater than 0.1 equivalents (up to 2 equivalents), the *ee* remained approximately constant.

For the carbonate bases we next tested the effect of the accompanying counterion, but little variation in

Table 1. Asymmetric epoxidation of 1-phenylcyclohexene mediated with H₂O₂ by catalyst **4**.

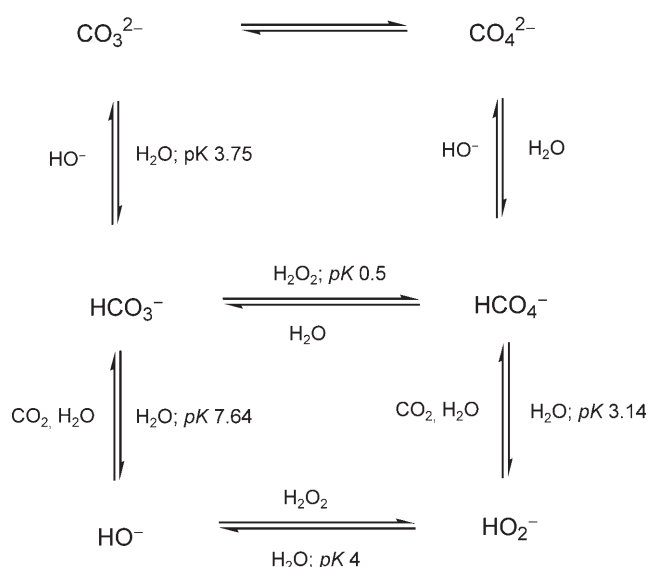
Entry ^[a]	Base	Equiv.	Temp. [°C]	Conv. [%] ^[b]	ee [%] ^[b]
1	Li ₂ CO ₃	0.2	0	29	19
2	LiOH	0.2	0	100	28
3	NaHCO ₃	0.01	0	<5	<5
4	NaHCO ₃	0.1	0	22	35
5	NaHCO ₃	0.2	0	63	33
6	NaHCO ₃	0.2	20	100	29
7	NaHCO ₃	1	0	34	35
8	NaHCO ₃	1	20	100	31
9	NaHCO ₃	2	0	35	35
10	NaHCO ₃	2	20	100	32
11	Na ₂ CO ₃	0.2	0	52	36
12	Na ₂ CO ₃	0.2	20	100	27
13	Na ₂ CO ₃	1	0	47	34
14	Na ₂ CO ₃	2	0	42	36
15	NaOH	0.2	0	100	28
16	KHCO ₃	0.2	0	19	35
17	KHCO ₃	0.2	20	57	32
18	K ₂ CO ₃	0.2	0	26	39
19	K ₂ CO ₃	0.2	20	96	34
20	KOH	0.2	0	58	34
21	Rb ₂ CO ₃	0.2	0	29	35
22	Rb ₂ CO ₃	0.2	20	75	31
23	Cs ₂ CO ₃	0.2	0	41	36
24	Cs ₂ CO ₃	0.2	20	89	30
25	NH ₄ HCO ₃	0.2	0	7	40

^[a] Epoxidation conditions: Iminium salt catalyst (10 mol%), H₂O₂ (50%, 6 equiv.), base, MeCN:H₂O (9:1), 24 h.

^[b] Conversions and enantiomeric excesses were determined from the chiral GC spectra by comparison of the alkene/epoxide and epoxide/epoxide peak areas respectively; the major enantiomer generated was the (1*S*,2*S*) epoxide.

the product *ee* was observed (36% *ee* for Cs₂CO₃, 35% *ee* for Ru₂CO₃, 39% *ee* for K₂CO₃, 31% *ee* for Na₂CO₃). Interestingly, similar levels of enantioselectivity were observed with rubidium and caesium carbonates despite increased background epoxidation in the absence of catalyst. Presumably the presence of an iminium salt catalyst offers a lower energy pathway, leading to asymmetric epoxidation.

In interpreting these observations it must be borne in mind that several equilibria determine the availability of the key species responsible for generating the oxaziridinium cations. The interrelation of these is shown in Scheme 3, in which are indicated *pK* values for some of the individual processes in water that can be deduced from literature values for the *pK_a* values of water, hydrogen peroxide and carbonic acid, together with that for the equilibrium in Eq. (1). It is clear that, at a fixed pH in the range 10–11, and a formal concentration of hydrogen peroxide of 1 M,

**Scheme 3.**

carbonate and percarbonate species will be present in roughly equal concentrations and the hydroperoxide ion concentration will be small, so that [HCO₄[−]]/[HOO[−]] is about 1000. Bearing in mind that hydrogen percarbonate anion can exist in two prototropic forms, HOO–CO–O[−] and HO–CO–OO[−], only the less stable of which (the latter) is expected to be an effective oxidising agent for the iminium cation, and that hydroperoxide anion may be intrinsically more reactive, the balance of reaction between Pathways A and B in Scheme 2 may be substantially less than 1000. Percarbonate and hydroperoxide anions can be expected to convert chiral iminium salts to the oxaziridinium species with different facial selectivities, giving different diastereoisomeric excesses. Since each diastereoisomeric oxaziridinium cation will have its own overall reactivity and enantioselectivity in transferring an oxygen atom to the alkene, the enantioselection observed in the epoxide produced in iminium ion-catalysed oxidation will clearly be dependent on the choice of oxidant. Different enantioselectivities may thus be anticipated from iminium ion-mediated oxygen transfer using as oxidant Oxone, hydrogen peroxide in the presence of a carbonate base, or peroxide anion (hydrogen peroxide plus a strong base capable only of deprotonating it).

The active oxidant in Oxone is KHSO₅, and so KHSO₄ was tested to determine if the hydrogen peroxide oxidant could oxidise the potassium salt to the active persulfate *in situ*, in the hope that this system might give similar enantioselectivity to the Oxone epoxidation system. Na₂SO₄, K₂SO₄ and KHSO₄ were used in test reactions, but only poor levels of conversion to the epoxide (<15%) were observed.

Table 2. Effect of temperature on the asymmetric epoxidation of 1-phenylcyclohexene mediated by catalysts **3** and **4**.^[a]

Entry	Catalyst	Temp. [°C]	Time [h]	Conv. [%] ^[b]	ee [%] ^[b]
1	3b	0	24	62	15
2	3b	0	7 days	100	13
3	3b	20	23	100	18
4	4	−10	24	19	35
5	4	−5	24	21	38
6	4	0	24	48	36
7	4	0	7 days	100	34
8	4	10	24	66	32
9	4	20	22	100	29
10	4	30	2.5	100	32

^[a] Epoxidation conditions: Iminium salt (10 mol%), H₂O₂ (50%, 6 equiv.), NaHCO₃ (0.2 equiv), MeCN:H₂O (9:1), 24 h.

^[b] Conversions and enantiomeric excesses were determined from the chiral GC spectra by comparison of the alkene/epoxide and epoxide/epoxide peak areas respectively; the major enantiomer generated was the (1*S*,2*S*)-epoxide.

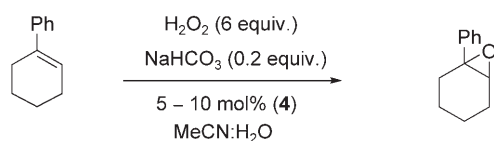
Effect of Temperature on the Reaction

We next investigated the effect of temperature on the enantioselectivity in epoxidation reactions carried out between −10 and 30 °C (Table 2). A small increase in enantioselectivity occurred as the temperature was reduced. As the temperature decreased the rate also decreased, requiring one week for the reaction to reach completion at 0 °C, whereas full conversion to the epoxide at 20 °C was observed in less than 24 h. At 30 °C, the reaction is complete after 2.5 h. Catalyst **4** showed increased levels of enantioselectivity over catalyst **3b**, but **3b** generally gave better conversion to the epoxide at lower temperatures.

Effects of Solvents on the Reaction

Effects of the Ratio of Co-solvents Used

Our first reactions were carried out using an acetonitrile:water (9:1) solvent system. We have investigated the effect of the proportion of water on the enantioselectivity of the epoxidation process (Scheme 4).

**Scheme 4.**

Reactions were carried out using six molar equivalents of H₂O₂ from a 50% aqueous solution; the results are shown in Table 3. In each case the volumes of water and hydrogen peroxide in the reagent were taken into account when determining the proportion of water present in the total solvent volume. A 0% water solvent system was achieved by the use of ethereal hydrogen peroxide.

Table 3 clearly shows that increasing the proportion of water present decreases the observed *ee* under these conditions. This is in sharp contrast to our aqueous Oxone system, in which *ee* is unaffected by the proportion of water, but in which the rate of reaction increases sharply as the proportion of water is increased.^[6b] Although many hours or even days may be required for these reactions to reach completion, the enantioselectivity of the epoxide product remains constant throughout this time. Maximum enantioselectivity was obtained under the anhydrous reaction conditions (56% *ee*); this is comparable to the Oxone-mediated system (60% *ee*), when using 1-phenylcyclohexene as the substrate and iminium salt **4** as catalyst.^[7] This effect of water content with respect to enantioselectivity may perhaps be interpreted in

Table 3. Asymmetric epoxidation of 1-phenylcyclohexene mediated by catalyst **4** with varying concentrations of acetonitrile and water solvent system.

Entry	H ₂ O [%]	Temp. [°C]	Time [h]	Conv. [%] ^[b]	ee [%] ^[b]
1 ^[d]	0 ^[c]	−5	7 days	100	56
2	0 ^[c]	0	24	39	42
3	0 ^[c]	20	24	100	45
5 ^[d]	13	−5	7 days	100	46
6	13	0	24	59	42
4	13	20	24	100	39
7	20	0	24	78	35
8	20	20	24	100	32
9	24	0	24	77	35
10	24	20	24	100	28
11	35	0	24	71	34
12	35	20	24	100	26
13	50	0	24	46	30
14	50	20	24	100	23
15	61	0	24	27	30
16	61	20	24	100	23

^[a] Epoxidation conditions: Iminium salt catalyst (10 mol%), H₂O₂ (50%, 6 equiv.), NaHCO₃ (0.2 equiv), MeCN:H₂O, 0 °C, 24 h.

^[b] Conversions and enantiomeric excesses were determined from the chiral GC spectra by comparison of the alkene/epoxide and epoxide/epoxide peak areas respectively; the major enantiomer was the (1*S*,2*S*)-epoxide in each case.

^[c] Ethereal hydrogen peroxide used; reaction volume contained 13% Et₂O.

^[d] K₂CO₃ used as base.

terms of water influencing the stereochemical course of the reaction by affecting the diastereofacial selectivity of addition of the peroxy anion to the iminium carbon atom (Pathway B, Scheme 2), for example, by diastereofacially selective co-ordination of water molecules to the electron-deficient iminium units. Changing the solvent will alter the equilibria shown in Scheme 3, perhaps slowing down the percarbonate generation relative to the fast proton transfers; thus hydroperoxide may become relatively more important than percarbonate, and this also might reduce enantioselectivity. Further, anions generally are less active in aqueous solvents than in dipolar aprotic ones, and this might retard the addition of percarbonate or hydroperoxide to the iminium ion.

Dissociation of the organic catalyst salt may also be a factor. In the iminium-BPh₄[−] ion pair, in low dielectric solvents where ion association is appreciable, the large anion would be expected to be positioned on the more accessible face of the iminium bond, so forcing reaction with the oxidant to occur at the other face. An increasing proportion of water would help to dissociate the salt into the individually solvated species, which would be expected to expose more of the face of the iminium salt previously blocked by the BPh₄[−] moiety, increasing the accessibility of that face to the oxidant. Diastereofacial selectivity in the formation of the oxaziridinium species would then be reduced. Electrostatic interaction between component ions in these ion pairs will, however, be small because of the large ionic radii, even in 90% acetonitrile, limiting the effect of this phenomenon.

Effects of Change of Organic Co-solvent

A range of reactions with different co-solvents was carried out using catalyst **4**, hydrogen peroxide, and potassium carbonate, at −5°C to prevent background epoxidation (Table 4).

It is worth noting that many of the experiments in Table 4 are multiphase. It appears that some solvents that provide a more homogeneous reaction mixture may increase the enantioselectivity of the epoxidation, for example acetone (53% *ee*) methanol (44% *ee*) and acetonitrile (37% *ee*).

Conclusions

We have successfully demonstrated the use of hydrogen peroxide as the stoichiometric oxidant in iminium salt-catalysed asymmetric epoxidation, providing a cheaper and greener alternative to Oxone. The reaction is promoted by a catalytic amount of an inorganic promoter such as carbonate, hydrogen carbonate and hydroxide. The enantioselectivity of the reaction is

Table 4. Asymmetric epoxidation of 1-phenylcyclohexene mediated by catalyst **4** in various solvent systems.^[a]

Entry	Co-solvent	Conv. [%] ^[b]	<i>ee</i> [%] ^[c]
1	Cyclohexane	26	32
2	Hexane	0	0
3	Toluene	0	0
4	Ether	27	27
5	Chloroform	0	0
6	Ethyl acetate	0	0
7	THF	53	30
8	Dichloromethane	0	0
9	Methyl isobutyl ketone	69	26
10	Acetone	5	53
11	Ethanol	12	0
12	Methanol	13	42
13	Acetonitrile	19	35.2

^[a] Epoxidation conditions: Iminium salt catalyst **4** (10 mol%), H₂O₂ (50%, 6 equiv.), K₂CO₃ (0.2 equiv.), solvent (1 mL), −5°C, 24 h.

^[b] Conversions were evaluated from the chiral GC spectra by comparison of the alkene and epoxide peak areas.

^[c] Enantiomeric excesses were determined by chiral GC spectra by comparison of the two epoxide peak areas; the major enantiomer generated was the (1*S*,2*S*) epoxide in each case.

generally lower than when using Oxone as oxidant, but is largely independent of the amount of base and catalyst, and the nature of cation associated with the base. In contrast, water content and temperature appear to have the greatest impact on the enantioselectivity and rate. We believe that this process operates through a double catalytic cycle, the promoter acting either as a base (hydroxide) or a peroxophore (carbonate) (Scheme 2).

Optimisation of the oxidative system enabled asymmetric epoxidation of 1-phenylcyclohexene with 56% *ee* utilising catalyst **4** and ethereal hydrogen peroxide in the absence of water at −5°C. Further work on alternative oxidants and catalysts with a view to developing more enantioselective systems is in progress.

Experimental Section

General Experimental Details

All infrared spectra were obtained using a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer; thin film spectra were acquired using sodium chloride plates. All ¹H and ¹³C NMR spectra were measured at 400.13 and 100.62 MHz, respectively, using a Bruker DPX 400 MHz spectrometer, in deuteriochloroform solution unless otherwise stated, using TMS (tetramethylsilane) as the internal reference. Mass spectra were recorded using a Jeol-SX102 instrument utilising electron-impact (EI), fast atom bombardment (FAB), or by the EPSRC national mass spectrometry service at the

University of Wales, Swansea. Optical rotation values were measured with an Optical Activity-polAAar 2001 instrument, operating at $\lambda = 589$ nm, corresponding to the sodium D line, at the temperatures indicated. All chromatographic manipulations used silica gel as the adsorbent. Reactions were monitored using thin layer chromatography (TLC) on aluminium-backed plates coated with Merck Kieselgel 60 F254 silica gel. TLC plates were visualised by UV radiation at a wavelength of 254 nm, or stained by exposure to an ethanolic solution of phosphomolybdic acid (acidified with concentrated sulfuric acid), followed by charring where appropriate. Reactions requiring anhydrous conditions were carried out using glassware dried overnight at 150 °C, under a nitrogen atmosphere unless otherwise stated. Reaction solvents were used as obtained commercially unless otherwise stated. Light petroleum (b.p. 40–60 °C) was distilled from calcium chloride prior to use. Ethyl acetate was distilled over calcium chloride. Dichloromethane was distilled over calcium hydride. Tetrahydrofuran and diethyl ether were distilled under a nitrogen atmosphere from the sodium/benzophenone ketyl radical. Acetone was dried over 4 Å Linde molecular sieve, and distilled under a nitrogen atmosphere. Enantiomeric excesses were determined either by proton nuclear magnetic resonance spectroscopy in the presence of europium(III) tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] as the chiral shift reagent, by chiral HPLC using a Chiracel OD column on a TSP Thermo-Separating-Products Spectra Series P200 instrument, with a TSP Spectra Series UV100 ultra-violet absorption detector set at 254 nm and a Chromojet integrator, or by chiral GC using a Chiraldex B-DM column on a Fisons GC8000 series instrument with a flame ionisation detector and a CE Instruments ChromeCard data station.

General Procedure for the Formation of Racemic Epoxides for *ee* Determinations

The alkene (1 equiv.) was dissolved in dichloromethane (10 mL g⁻¹) and cooled to 0 °C. *m*-CPBA (2 equiv.) was added as a solution also in dichloromethane (10 mL g⁻¹). The reaction mixture was allowed to attain ambient temperature and stirred until complete consumption of the substrate was observed by TLC. The reaction was quenched with the addition of saturated aqueous NaHCO₃ (10 mL g⁻¹) and the layers separated. The organic layer was washed with saturated NaOH (1.0 M) (10 mL g⁻¹) and dried (MgSO₄). Solvents were removed under reduced pressure. The pure epoxide was obtained after column chromatography eluting with ethyl acetate/light petroleum (1:99).

General Procedure for Catalytic Asymmetric Epoxidation of Simple Alkenes Mediated by Iminium Salts using Oxone

Oxone (2 equiv.) was added to an ice-cooled solution of sodium carbonate (4 equiv.) in water (12 mL per 1.50 g of sodium carbonate), and the resulting foaming solution stirred for 5–10 min. The iminium salt (10 mol%) was added as a solution in acetonitrile (6 mL per 3.6 mmol of alkene), followed by the alkene substrate (1 equiv.), also as a solution in acetonitrile of the same volume as the solution of the catalyst. The mixture was stirred at 0 °C until the substrate was

completely consumed (TLC analysis). The reaction mixture was diluted with ice-cooled diethyl ether (20 mL per 100 mg substrate) followed by the same volume of water. The aqueous phase was washed four times with diethyl ether, and the organic solutions combined, washed with brine, and dried (MgSO₄). Filtration and evaporation of the solvents gave a yellow/brown residue. The pure epoxide was obtained after column chromatography, eluting with ethyl acetate/light petroleum (1:99).

General Procedure for Catalytic Asymmetric Epoxidation of Simple Alkenes Mediated by Iminium Salts using Hydrogen Peroxide and Bicarbonate Salts

The bicarbonate salt (0.2 equiv.) and the iminium salt catalyst (10 mol%) were added to acetonitrile (1 mL), and the mixture cooled to –5 °C. The substrate alkene (1 equiv.) was added, and the mixture allowed to reach equilibrium. Hydrogen peroxide (6 equiv.) was added. The reaction mixture was stirred vigorously and monitored by TLC. After a maximum of 24 h except where indicated, ice-cold brine was added, followed by ice-cooled diethyl ether (20 mL per 100 mg substrate). The aqueous phase was washed four times with diethyl ether, and the organic solutions combined and dried (MgSO₄). Filtration and evaporation of the solvents gave a yellow/brown residue. The pure epoxide was obtained after column chromatography, eluting with ethyl acetate/light petroleum (1:99).

General Procedure for the Background Epoxidation Reaction with Hydrogen Peroxide and Bicarbonate Salts in the Absence of Iminium Salt Catalyst

The bicarbonate salt (0.2 equiv.) was dissolved in acetonitrile (1 mL), and the solution cooled to –5 °C. The substrate alkene (1 equiv.) was added, and the mixture allowed to reach equilibrium. Hydrogen peroxide (6 equiv.) was added. The reaction mixture was stirred vigorously and monitored by TLC. After 24 h, brine was added, the mixture extracted with diethyl ether, and the ethereal layer dried (MgSO₄). Filtration and evaporation of the solvents gave the crude product mixture. Analysis by chiral GC-FID showed less than 5% conversion to the epoxide (conversion was evaluated by comparison of the epoxide versus the alkene peak areas).

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