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Exocyclic Iminium Salts as Catalysts for Alkene Epoxidation by Oxone®

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Abstract

Exocyclic iminium salts are evaluated as catalysts for alkene epoxidation by Oxone®, presumed to proceed *via* the corresponding oxaziridinium species. Iminium triflate salts derived from pyrrolidine and electron poor aromatic aldehydes were found to be good catalysts. Attempts to prepare chiral variants of these iminium salts were largely unsuccessful, presumably due to their ready hydrolysis.

Keywords: Iminium salts; epoxidation; oxaziridines; catalysts

Introduction

The development of catalytic methods for the asymmetric epoxidation of unfunctionalised alkenes (*i.e.* those lacking functionality for coordination to the reagent) remains an important goal in synthesis [1]. The chiral manganese salen complexes developed independently by Jacobsen and by Katsuki provide excellent enantioselectivity for *cis*-disubstituted olefins [1]. More recently, some of the most impressive advances have been in the catalysis of alkene epoxidation by Oxone® [2-8], with the chiral ketones developed by Shi and co-workers [4,5] providing particularly high enantioselectivities (*via* chiral dioxiranes) for epoxidation of trisubstituted and *trans*-alkenes. One problem with chiral dioxiranes is that due to the divalency of oxygen, they possess an "achiral region" remote from the chiral substituents on the ring carbon. It might be expected that replacement of one of the ring oxygens with a nitrogen atom

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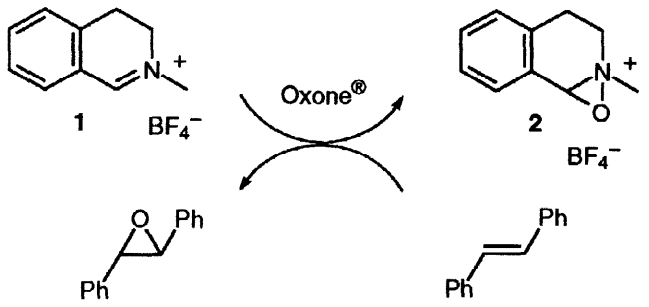
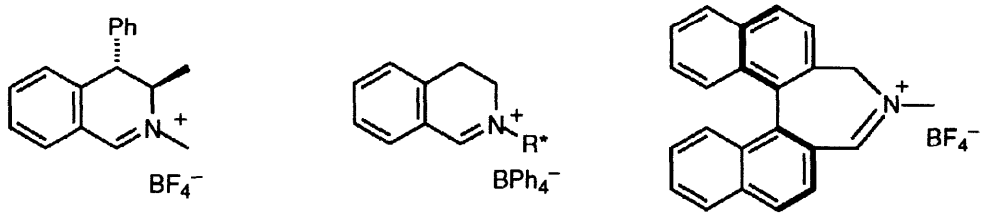
would allow greater flexibility in the design of chiral catalysts. We were therefore attracted to the pioneering work of Hanquet and Lusinchi and co-workers on the chemistry of oxaziridinium salts [9-12]. These workers demonstrated a catalytic cycle where iminium salts (*e.g.* **1**) could be converted by Oxone® into the corresponding oxaziridinium species **2** which could effect alkene epoxidation (Scheme 1) [10]. In a preliminary investigation of the use of chiral oxaziridinium salts for asymmetric epoxidation, a promising result of 33% ee was obtained for epoxidation of *E*-stilbene using (+)-norephedrine-derived chiral iminium salt **3** [11]. Page and co-workers have recently reported the synthesis and evaluation of a range of dihydroquinoline derivatives with various chiral groups attached to the nitrogen, obtaining enantioselectivities of up to 73% ee with catalysts **4** [13]. Additionally, Aggarwal has reported the novel chiral iminium salt **5** [14] (31% ee for epoxidation of *E*-stilbene; 71% ee for the epoxidation of 1-phenylcyclohexene).



Scheme 1

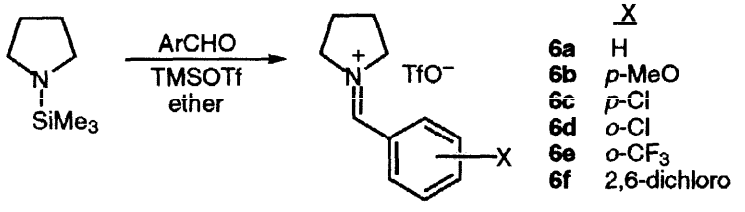


3 **4** **5**

All of the iminium salts used to date as epoxidation catalysts have the iminium bond as part of a ring (endocyclic iminiums), and are therefore effectively derived from intramolecular condensation of a carbonyl compound and an amine. This places a limitation on the number of iminium salts (particularly chiral ones) that can be synthesised and evaluated as epoxidation catalysts. We were therefore interested in examining iminium salts derived from intermolecular condensation of a separate amine and carbonyl compound (*i.e.* exocyclic iminium salts). Such an approach would allow greater diversity in reagent preparation from a range of chiral amines and carbonyl compounds, and potentially allow a combinatorial approach to reagent discovery. We report here our work towards this goal [15].

Results and discussion

An initial concern was that simple exocyclic iminium salts might prove too sensitive to hydrolysis to be useful as epoxidation catalysts. A literature search for exocyclic iminium salts that might be easily prepared uncovered a report by Leonard in 1963 that iminium perchlorate salts could readily be prepared from pyrrolidine perchlorate and aromatic aldehydes under Dean-Stark conditions [16], and iminium salts of this type therefore appeared to be a suitable starting point. However, our initial experiments revealed difficulties in obtaining crystalline products in some examples; additionally, we wished to avoid the use of potentially explosive perchlorate salts and also desired a more rapid method of iminium synthesis. Thus, following the recently described procedure of Schroth and co-workers [17, 18], we prepared a range of simple iminium salts **6** by reaction of commercially available *N*-trimethylsilylpyrrolidine (1 eq) and an aromatic aldehyde (1 eq) with trimethylsilyl triflate (1 eq) in ether (Scheme 2). Here, the iminium product precipitates instantly from the reaction mixture and can be isolated by filtration. The products proved to be sensitive to moisture, but we found that they were stable over several weeks if stored in a desiccator. Iminium triflates **6a** and **6b** were obtained in analytically pure form by recrystallisation from EtOAc. Unfortunately, we were unable to purify iminium salts **6c-6f** by recrystallisation and so the samples used were contaminated with pyrrolidine triflate (up to 30%). The purity of each catalyst was estimated by ^{1}H NMR and the amount used in the epoxidation experiments was corrected to compensate for the presence of pyrrolidine triflate. Epoxidation reactions were performed using the Oxone® / CH_3CN / H_2O system described by Lusinchi, Hanquet and co-workers [10]. Control experiments established that pyrrolidine triflate itself did not catalyse the Oxone® epoxidation. Although the starting iminium salts did not contain the parent aldehydes, the latter could conceivably be present in the reaction mixture due to iminium hydrolysis. We therefore also verified that no epoxidation occurred when *o*-chlorobenzaldehyde (1 equivalent) was used in place of an iminium salt.



Scheme 2

As a test reaction, we examined the iminium salts **6** as catalysts for the epoxidation of *E*-stilbene by Oxone® in CH_3CN / H_2O. The results are given in Table 1. Conversion to *E*-stilbene oxide was measured after 4 hours in each case; longer reaction times did not generally result in increased conversions, presumably due to decomposition of the catalyst by hydrolysis. Indeed, stirring the solution of the olefin, iminium salt and $NaHCO_3$ for *ca.* 10 minutes prior to addition of Oxone® led to no epoxidation, indicating that the catalyst had been destroyed.

The iminium salts **6** were first tested in stoichiometric quantities (entries 1-4). The

benzaldehyde-derived iminium salt **6a** was a poor promoter (25% conversion after 4 hours, entry 1) while, strikingly, the methoxy-substituted compound **6b** was totally inactive (entry 2). Far better (entries 3 and 4) were the chloro-compounds **6c** and **6d**; the *ortho*- isomer **6d** effected complete conversion. The *ortho*-chloro compound **6d** proved to be effective at lower catalyst loadings (entries 5 to 7): conversion was still high (82%) when 10 mol% was used (entry 6), but moderate (52%) when 5 mol% was used (entry 7). The *para*-chloro isomer **6c** was clearly inferior (compare entries 6 and 8). Amongst other iminium salts of this type with *ortho*-electron withdrawing groups, the best we found was the *ortho*-trifluoromethyl compound **6e** (entries 9 and 10), which gave slightly better results than **6d**. The improved conversions with the electron poor iminium salts can be attributed either to increased rate of attack on the iminium salt by Oxone®, or to faster electrophilic epoxidation by the resulting oxaziridinium species. The exact reason for the superior performance of the *ortho*-isomers is unclear at present, but it may be related to the lower tendency for the aromatic ring to adopt planarity with respect to the iminium bond, thus resulting in a loss of conjugation. Incorporation of a second *ortho*-electron withdrawing group did not prove beneficial, however; the 2,6-dichloro compound **6f** is inferior to **6d** (compare entries 6 and 11). This may reflect increased steric hindrance, or increased susceptibility to hydrolysis.

Table 1

Epoxidation of *E*-stilbene with Oxone® catalysed by iminium salts **6**[a]

Entry	Iminium	Mol % **6**	Conversion (%)[b]
1	**6a**	100	25
2	**6b**	100	0
3	**6c**	100	63
4	**6d**	100	100
5	**6d**	25	100
6	**6d**	10	82
7	**6d**	5	52
8	**6c**	10	24
9	**6e**	10	100
10	**6e**	5	52
11	**6f**	10	28

[a]*E*-Stilbene (0.63 mmol), $NaHCO_3$ (2.50 mmol), iminium salt, acetonitrile (6 ml), water (25 μl), Oxone® (1.25 mmol $KHSO_5$). [b]Conversion to epoxide, estimated by ^1H NMR spectroscopic integration.

Having identified the *ortho*-trifluoromethyl compound **6e** as the best epoxidation catalyst among the simple iminium salts we studied, we then investigated its use for the epoxidation of

a range of other alkenes (Table 2). As reported by Aggarwal [14], reaction is fastest for more highly substituted alkenes (hence the regioselective epoxidation of limonene and the poor conversion for styrene). We have investigated some other important fundamental aspects of this chemistry and these results are also included in Table 2. Epoxidation of *Z*-stilbene provided *cis*-stilbene oxide stereospecifically (entry 6), thus suggesting that the epoxidation is a concerted process. Epoxidation of 2-cyclohexenol afforded a mixture of diastereomers (entry 7), indicating the absence of any hydroxyl directing effect. This is in accord with previous observations using endocyclic iminium salts [12]. Electron poor olefins were examined as substrates: *E*-chalcone showed <2% conversion over 4 hours (entry 8), while *E*-ethyl cinnamate did not react (entry 9).

We made several attempts to observe or isolate oxaziridinium salts derived from iminium salts **6** (for example by reaction with *m*CPBA as described by Lusinchi and Hanquet [12]), but these were not successful.

Table 2

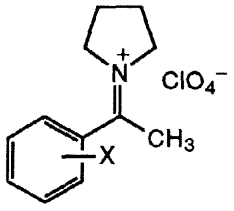
Oxone® Epoxidation of Alkenes Catalysed by Iminium salt **6e**[a]

Entry	Alkene	Conversion[b]	Isolated yield[c] (%)
1	*E*-Stilbene	100	89
2	*E*-α-Methylstilbene	97	92
3	1-Phenylcyclohexene	98	93
4	Limonene	87[d]	72
5	Styrene	50	38
6	*Z*-Stilbene	78[e]	50
7	2-Cyclohexenol	100[f]	-
8	*E*-Chalcone	< 2	-
9	*E*-Ethyl cinnamate	0	-

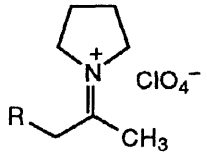
[a]Alkene (0.63 mmol), $NaHCO_3$ (2.50 mmol), **6e** (10 mol%), acetonitrile (6 ml), water (25 μl), Oxone® (1.25 mmol $KHSO_5$). [b]Estimated by ^1H NMR spectroscopic integration. [c]Isolated yield of epoxide product. [d]Epoxidation exclusively on ring alkene, 70:30 ratio of diastereomers. [e]*Cis*-epoxide only. [f]Syn:anti ratio = 53:47.

Before attempting the synthesis of chiral iminium salts, some further exploratory work was performed to establish the structural variation in the iminium that would be tolerated. Investigating briefly the amine component, attempts to replace the pyrrolidine moiety in **6e** with morpholine, piperidine or diethylamine in the TMSOTf procedure provided small amounts of triflate salts which underwent hydrolysis too rapidly to allow their screening as epoxidation catalysts. Returning to pyrrolidine as the amine, the carbonyl portion was varied

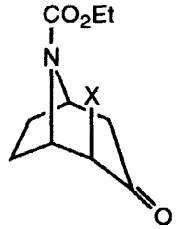
next. To date, there have been no literature reports on oxaziridinium epoxidation using *ketone*-derived iminium salts, whether endo-or exocyclic, so we deemed this worthy of investigation. However, no iminium salt was obtained in the reaction of trimethylsilylpyrrolidine and TMSOTf with acetone, acetophenone, trifluoromethylacetophenone, or benzophenone. The known [16] iminium perchlorate salt **7a** was prepared from pyrrolidine and acetophenone under Dean-Stark conditions, but it failed to promote epoxidation of *E*-stilbene (0% conversion after 4 hours using 1 equivalent of **7a**). Following the strategy that we had previously found to be successful with aromatic aldehydes, we prepared the *ortho*-chloro-substituted iminium perchlorate **7b**, which indeed proved to be a better (but moderate) epoxidation promoter (41% epoxidation of *E*-stilbene after 4 hours using 1 equivalent **7b**).[1] Turning to aliphatic ketones, the acetone-derived iminium perchlorate **8** [16] was readily prepared simply by adding pyrrolidine perchlorate to acetone; this iminium salt (1 equivalent) effected 53% epoxidation of *E*-stilbene after 4 hours. We next attempted to improve the catalytic efficiency by placing an electron withdrawing substituent α- to the carbonyl. α-Acetoxyacetone indeed provided (Dean-Stark conditions) a more effective iminium perchlorate **9** (88% epoxidation of *E*-stilbene after 4 hours using 1 equivalent of **9**).[1] This is a promising result, suggesting that electronically activated aliphatic ketones might provide good iminium catalysts. However, there appeared to be few readily available, activated ketones containing functionality that is likely to tolerate the iminium formation conditions. In work in the related dioxirane area, we recently reported success using *N*-carbethoxytropinone **10** as a catalyst for Oxone® epoxidation [8]. Pleasingly, we were able to prepare and fully characterise the iminium perchlorate **12** derived from **10** and pyrrolidine. Again, compound **12** was a moderate promoter (37% epoxidation of *E*-stilbene after 4 hours using 1 equivalent of **12**). We turned next to derivatives of the fluoroketone **11**, which is further activated electronically and is an efficient and conformationally well-defined dioxirane precursor [8]. However, all attempts to prepare iminium salt **13** from **11** have been unsuccessful, presumably due to the acidity of the proton α-to fluorine and / or ready hydrolysis. Indeed, our other preliminary attempts to prepare iminium salts from readily available chiral ketones (*e.g.* camphor) were also unsuccessful.



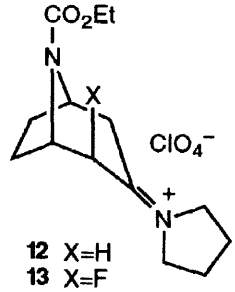
7a X=H
7b X=*o*-Cl



8 R=H
9 R=OAc



10 X=H
11 X=F

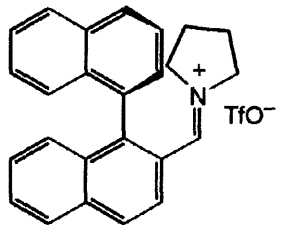


12 X=H
13 X=F

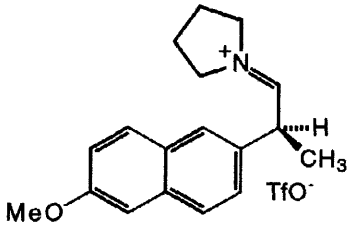
[1] In control experiments, we established that there was no epoxidation of *E*-stilbene under these conditions in the presence of 1 equivalent of either *o*-chloroacetophenone or α-acetoxyacetone in place of the iminium salt. α-Acetoxyacetone has been shown by Yang [2] to be an efficient catalyst for alkene epoxidation (*via* the corresponding dioxirane) in a related Oxone® / CH_3CN / H_2O system, but it should be noted that the Yang system employs a 3:2 CH_3CN / H_2O mixture, whereas the iminium catalytic system employed here contains very little water.

Attempting to prepare analogues of compounds **6** with chiral aldehydes in place of benzaldehyde, we first investigated synthesis of the novel iminium salt **14**. Using the TMSOTf method, we did obtain a sample of **14** but it was of very low purity and was not active at all as an epoxidation catalyst. This has discouraged us to date from attempting to prepare analogues of **14** bearing electron withdrawing substituents.

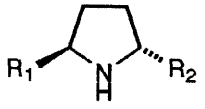
Use of α-chiral aldehydes, potentially problematic due to epimerisation, was also briefly examined. An impure sample of the novel chiral iminium salt **15** was prepared by the TMSOTf method; in the epoxidation of *E*-stilbene, the reactivity was moderate (44% conversion after 4 hours with 1 equivalent of iminium) and the enantioselectivity low (9% ee). In view of this disappointingly low selectivity, and bearing in mind the likely difficulty in improving it through synthetically simple rational structural alterations, this system was not pursued further.



14



15



16 R_1=CH_3, R_2=H
17 R_1=R_2=CH_3
ent-18 R_1=$C(OCH_3)Ph_2$, R_2=H
ent-19 R_1=$C(OCH_3)(CH_3)_2$, R_2=H
ent-20 R_1=CH_2OCH_3, R_2=H

We spent some time trying to incorporate chiral, substituted pyrrolidines into compounds similar to **6**. The known chiral amines **16** to **20** were selected for screening. However, we encountered considerable difficulties in trying to convert these hindered α-substituted pyrrolidines to the *N*-silyl derivatives required for our preferred method for iminium formation. Using pyrrolidine itself as a model, we managed to develop a procedure for silylation of the amine (K_2CO_3, TMSCl, benzene, reflux) and this crude silylated amine could then be converted into the iminium triflate **6d** in the usual way. Attempts to extend this protocol to amines **17**-**19** and *o*-chlorobenzaldehyde were unsuccessful, however. With amine **20** and *o*-trifluoromethylbenzaldehyde, a small amount of iminium was evident in the crude ^1H NMR spectrum (iminium proton at *ca.* 9.2 ppm), but this crude material afforded low enantioselectivity (10% ee) for the epoxidation of *E*-stilbene. Under Dean-Stark conditions, we did manage to obtain a crude sample of the iminium perchlorate salt derived from **16** and *o*-chlorobenzaldehyde; however, epoxidation of *E*-stilbene with a stoichiometric amount of this salt proceeded in low conversion (9%) and enantioselectivity (15% ee). Slightly better results were obtained with this crude iminium salt (1 equivalent) and 1-phenylcyclohexene (100% conversion, 22% ee). The difficulty in obtaining a sufficiently pure sample of this iminium for reliable testing meant that we did not investigate this compound further. We obtained no iminiums under Dean-Stark conditions in the reaction of *o*-chlorobenzaldehyde with the perchlorate salts of amines **17** and **18**, or in the reaction of *o*-trifluoromethylbenzaldehyde with amine **19**. Thus, overall we have been unsuccessful to date in preparing stable chiral analogues of the iminium salts **6**.

Conclusions

We have shown for the first time that exocyclic iminium salts can be used as catalysts for alkene epoxidation with Oxone®, and we have also demonstrated that electronic effects can influence their reactivity. Iminium salts derived from pyrrolidine and aromatic aldehydes with electron withdrawing substituents in the *para*- or (particularly) the *ortho*-position were by far the most successful class that we used. However, extension to the use of more hindered, chiral amines was unsuccessful due to the ready hydrolysis of the iminium salts and / or the low reactivity of the oxaziridiniums. Moreover, the few chiral iminiums we did manage to prepare afforded low epoxide enantioselectivities.

We have also described the first examples of the use of ketone-derived iminium salts as promoters of epoxidation. Incorporation of electron withdrawing substituents again improved activity: iminium salts **7b**, **9** and **12** afforded moderate to good conversion, albeit in stoichiometric quantities.

Experimental

General

All NMR spectra were recorded in $CDCl_3$ unless otherwise stated, on a Bruker AM400, Bruker WM250 or a Jeol EX270 spectrometer. *J* values are given in Hz. IR spectra were recorded on a Perkin-Elmer 1605 FTIR spectrometer. FAB mass spectra were recorded on a VG AutoSpec machine. Elemental analyses were determined at the University of Bath or the University of Nottingham. Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Diethyl ether (referred to throughout as ether) was distilled from sodium-benzophenone ketyl; acetonitrile was distilled from calcium hydride. $CDCl_3$ was filtered through basic alumina before use. All commercial reagents were used without further purification unless stated otherwise.

Preparation of iminium salts

General procedure for the preparation of iminium triflate salts: To a solution of the aldehyde (5.0 mmol) in ether (15 ml) under nitrogen was added trimethylsilyl triflate (0.90 ml, 5.0 mmol), followed by *N*-trimethylsilyl pyrrolidine (0.87 ml, 5.0 mmol). The product iminium salt immediately began to precipitate. The reaction was stirred at room temperature for 4 hours, and the product collected by filtration under nitrogen. The solid product was washed with ether (3 x 10 ml) and dried under reduced pressure. The iminium was characterised by IR (ν_{max} *ca.* 1660 cm^{-1}) and ^1H NMR (iminium proton at *ca.* 9.2 ppm). Pyrrolidine triflate (^1H NMR peaks at 3.35 (br) and 2.04 (br)) was in some cases present as an impurity.

1-Benzylidenepyrrolidinium triflate **6a:** Using the above procedure with benzaldehyde gave the iminium salt **6a** (1.48g, 96%), as a colourless solid, mp 69°C (EtOAc); (Found: C, 46.50; H, 4.62; N, 4.45. $C_{12}H_{14}NSO_3F_3$ requires C, 46.6; H 4.56; N 4.53%); ν_{max} (nujol) 1660, 1596, 1152, 1032, 760 cm^{-1}; δ_H (250MHz) 9.29 (1H, s), 8.00-7.60 (5H, m), 4.48 (2H, t, *J* 7.0), 4.26 (2H, t, *J* 7.0), 2.40-2.15 (4H, m); δ_C (100MHz) 168.2, 136.2, 133.4, 129.7, 127.6, 60.2, 54.2, 25.4, 23.2; *m/z* (FAB+) 160 ($C_{11}H_{14}N^+$, 100%); (FAB-) 149 (CF_3O_3S, 100).

1-(4-Methoxybenzylidene)pyrrolidinium triflate **6b:** Using the above procedure with 4-methoxybenzaldehyde gave the iminium salt **6b** (1.46g, 86%) as a colourless solid, mp 93°C (EtOAc); (Found: C, 46.02; H, 4.82; N, 3.92. $C_{13}H_{16}NO_4SF_3$ requires C, 46.02; H 4.75; N 4.13%); ν_{max} (film) 1651, 1598, 1459, 1155, 1026, 844 cm^{-1}; δ_H (250MHz) 9.05 (1H, s), 7.97 (2H, d, *J* 9.0), 7.09 (2H, d, *J* 9.0), 4.38 (2H, t, *J* 7.1), 4.17 (2H, t, *J* 7.1), 3.94 (3H, s), 2.35-2.12 (4H, m); δ_C (100MHz) 165.6, 137.1, 120.1, 115.6, 59.8, 56.1, 53.5, 25.7, 23.4; *m/z* (FAB+) 190 ($C_{12}H_{16}NO^+$, 100%); (FAB-) 149 (CF_3O_3S, 100).

Pyrrolidinium triflate **6c:** Using the above procedure with 4-chlorobenzaldehyde gave 0.92g of a colourless solid containing the iminium salt **6c** contaminated with *ca.* 4mol% pyrrolidine triflate by ^1H NMR spectroscopy; ν_{max} (nujol) 1657, 1590, 1159, 1096, 1030, 847 cm^{-1}; δ_H (250MHz) 9.21 (1H, s), 7.90 (2H, d, *J* 8.7), 7.55 (2H, d, *J* 8.7), 4.41 (2H, t, *J* 7.0), 4.22 (2H, t, *J* 7.0), 2.35-2.22 (4H, m); δ_C (100MHz) 167.2, 143.3, 134.7, 130.2, 126.0, 60.3, 54.2, 25.5, 23.3; *m/z* (FAB) 194 (M^+, 100%), 72 ($C_4H_{10}N^+$, 7). (Observed M^+-OTf 194.0754. $C_{11}H_{13}NCl$ requires 194.0737).

Pyrrolidinium triflate **6d**: Using the above procedure with 2-chlorobenzaldehyde gave 1.32g of a colourless solid containing the iminium salt **6d** contaminated with *ca.* 14mol% pyrrolidine triflate by ^1H NMR spectroscopy; ν_{max} (nujol)1655, 1588, 1260, 1215, 1165, 1142, 1055, 1034, 775 cm^{-1}; δ_H (250MHz, CD_3CN) 9.20 (1H, t, *J* 1.8), 7.88 (1H, d, *J* 7.8), 7.81-7.58 (3H, m), 4.36 (2H, br s), 4.15 (2H, br s), 2.20-2.10 (4H, m); *m/z* (FAB) 194 (M^+, 100%). (Observed M^+-OTf 194.0752. $C_{11}H_{13}NCl$ requires 194.0737).

Pyrrolidinium triflate **6e**: Using the above procedure with 2-(trifluoromethyl)benzaldehyde gave 1.29g of a colourless solid containing the iminium salt **6e** contaminated with *ca.* 24mol% pyrrolidine triflate by ^1H NMR spectroscopy; ν_{max} (nujol) 1678, 1604, 1582, 1160, 1128, 1030, 773, 638 cm^{-1}; δ_H (250MHz, CD_3CN) 9.32 (1H, br d, *J* 2.1), 8.02-7.70 (4H, m), 4.39 (2H, t, *J* 6.6), 4.04 (2H, br s), 2.15 (4H, br s); *m/z* (FAB) 228 (M^+, 100%). (Observed M^+-OTf 228.1002. $C_{12}H_{13}F_3N$ requires 228.1000).

Pyrrolidinium triflate **6f:** Using the above procedure with 2,6-dichlorobenzaldehyde gave 1.64g of a colourless solid containing the iminium salt **6f** contaminated with *ca.* 14mol% pyrrolidine triflate by ^1H NMR spectroscopy; ν_{max} (nujol) 1685, 1584, 1562, 1439, 1274,

1252, 1224, 1152, 1028, 948, 784, 637 cm^{-1}; δ_H (250MHz, CD_3CN) 9.30 (1H, t, *J* 2.2), 7.77-7.46 (3H, m), 4.49 (2H, t, *J* 7.1), 3.96 (2H, br s), 2.31-2.10 (4H, m); *m/z* (FAB) 228 (M^+, 100%). (Observed M^+-OTf 228.0352. $C_{11}H_{12}NCl_2$ requires 228.0347).

Pyrrolidinium triflate **15:** Using the above procedure with (*S*)-(+)-2-(6-methoxy-2-napthyl)propionaldehyde [19] gave 1.65g of a colourless solid containing the iminium salt **15** contaminated with *ca.* 11mol% pyrrolidine triflate by ^1H NMR spectroscopy; ν_{max} (nujol) 1690, 1636, 1608, 1504, 1392, 1265, 1217, 1151, 1032, 850, 814, 754, 722, 638 cm^{-1}; δ_H (400MHz, CD_3CN) 8.49 (1H, m), 7.97-7.79 (3H, m), 7.44 (1H, dd, *J* 8.5, 1.9), 7.30 (1H, d, *J* 2.5), 7.20 (1H, dd, *J* 9.0, 2.5), 4.25 (1H, m), 4.15-3.85 (4H, m), 3.91 (3H, s), 2.17 (4H, br s), 1.65 (3H, d, *J* 7.0); *m/z* (FAB) 268 (M^+, 100%). (Observed M^+-OTf 268.1727. $C_{18}H_{22}NO$ requires 268.1701).

Preparation of iminium triflate ***6d*** via *silylation of pyrrolidine*

A mixture of pyrrolidine (0.71 g, 10 mmol), chlorotrimethylsilane (2.56 ml, 20 mmol) and potassium carbonate (1.38 g, 10 mol) in dry benzene (15 ml) was heated at reflux overnight under nitrogen. The solvent was then removed under reduced pressure to leave an oil, which was taken up in dry ether (30 ml). To a portion of the above solution (15 ml) were added successively 2-chlorobenzaldehyde (0.56 ml, 5 mmol) and TMSOTf (0.96 ml, 5.0 mmol). The mixture was stirred at room temperature for 3 hours, during which time a white precipitate formed. The solid was filtered, washed with dry ether (5 ml) and dried *in vacuo*, leaving a pale yellow solid (1.25 g, 73%) which ^1H NMR spectroscopic analysis indicated to be iminium **6d** of *ca.* 97% purity.

Iminium Perchlorate salts: Iminium perchlorate salts were prepared under Dean-Stark conditions using the procedure of Leonard [16]. Acetone and acetophenone iminium perchlorates (**7a** and **8**) have been described previously [16].

Iminium perchlorate **7b**: Reaction of pyrrolidine perchlorate (0.43g, 2.5 mmol) and *ortho*-chloroacetophenone (0.65ml, 5.0 mmol) in benzene (5 ml) under Dean-Stark conditions afforded a dark red oil which was recrystallised once from CH_3CN/Et_2O to give 0.3g of a dark red solid containing the iminium salt **7b** contaminated with *ca.* 11mol% pyrrolidine perchlorate by ^1H NMR spectroscopy; ν_{max} (nujol) 1669, 1590, 1316, 1270, 1081, 969, 920, 781, 722, 681, 621 cm^{-1}; δ_H (400 MHz, CD_3CN) 7.65-7.51 (4H, m), 4.19-4.16 (2H, m), 3.73-3.68 (2H, m), 2.74 (3H, s), 2.28-2.20 (2H, m), 2.10-2.05 (2H, m); δ_C (68 MHz, CD_3CN) 182.8 (s), 135.0 (s), 134.7 (d), 131.9 (d), 130.1 (s), 129.8 (d), 128.3 (d), 58.6 (t), 56.8 (t), 26.9, (q), 25.9 (t), 25.6(t); *m/z* (CI) 207 (M-H, 100%), 172 (M-HCl, 99.8%). (Observed M-$HClO_4$ 207.0811. $C_{12}H_{14}NCl$ requires 207.0815).

Iminium perchlorate **9**: Reaction of pyrrolidine perchlorate (0.43g, 2.5 mmol) and α-acetoxyacetone (0.58g, 0.50 mmol) in benzene (18 ml) under Dean-Stark conditions gave 0.23

g of a solid containing the iminium salt **9** contaminated with *ca.* 17mol% pyrrolidine perchlorate by ^{1}H NMR spectroscopy; ν_{max} (nujol) 1756, 1684, 1230, 1094, 978, 916, 866, 839, 741, 674, 624 cm^{-1}; δ_H (250MHz, CD_3CN) 5.44 (2 H, s), 3.92 (2H, br s), 3.85 (2H, br s), 2.38 (3H, s), 2.16 (4H, br s), 2.07 (3H, s); *m/z* (FAB) 170 (M^+, 100%). (Observed M^+-ClO_4 170.1173. $C_9H_{16}NO_2$ requires 170.1181).

Iminium perchlorate **12**: Reaction of pyrrolidine perchlorate (214 mg, 1.25 mmol) and *N*-ethoxycarbonyl tropinone (246 mg, 1.25 mmol) under Dean-Stark conditions provided the iminium perchlorate **12** (225 mg, 51%) as a colourless solid; mp 239-241°C (2-propanol); (Found: C, 47.91; H, 6.69; N, 7.94. $C_{14}H_{23}N_2O_6Cl$ requires C, 47.98; H, 6.62; N, 8.0%); ν_{max} ($CHCl_3$) 2965, 2888, 1697, 1655, 1424, 1345, 1324, 1306, 1272, 1237, 1210, 1118, 1075, 1021, 972 cm^{-1}; δ_H (250MHz) 4.55 (2H, br s), 4.20-4.11 (4H, m), 3.77 (2H, br s), 3.20-2.84 (4H, m), 2.50-1.89 (8H, m), 1.28 (3H, t, *J* 7.1); δ_C (68MHz) 184.8 (s), 153.5 (s), 61.7 (t), 54.4 (t), 50.6 (d), 40.6 (t), 29.3 (br t), 24.1 (t), 14.5 (q); *m/z* (FAB) 251 (M^+, 100%).

Pyrrolidinium perchlorate derived from amine **16**: Reaction of 2-methylpyrrollidine perchlorate (0.49g, 2.64 mmol) and 2-chlorobenzaldehyde (0.74g, 5.28 mmol) under Dean-Stark conditions afforded 0.59g of a solid containing iminium salt contaminated with *ca.* 15mol% pyrrolidine perchlorate by ^{1}H NMR spectroscopy; ν_{max} (nujol) 1599, 1105, 927, 722, 623 cm^{-1}; δ_H (400MHz, CD_3CN) 9.15 (1H, br s), 8.11-7.61 (4H, m), 4.60 (1H, m), 4.20 (2H, br s), 2.19-1.89 (4H, m), 1.61 (3H, d, *J* 5.8).

Typical Procedure for Alkene Epoxidation: *Epoxidation of E-stilbene catalysed by the iminium salt* **6e**

To a suspension of *E*-stilbene (0.113 g, 0.63 mmol), sodium bicarbonate (214 mg, 2.50 mmol) and the iminium salt **6e** (32 mg @ 76mol% purity, 0.0645 mmol iminium) in acetonitrile (6 ml) and water (25 µl) was added *immediately* Oxone® (384 mg, 1.25 mmol $KHSO_5$). After stirring at room temperature under nitrogen for 4 hours, water (10 ml) and CH_2Cl_2 (10 ml) were added. The aqueous layer was re-extracted with CH_2Cl_2 (3 x 10 ml) and the combined organics dried ($MgSO_4$), filtered and evaporated to yield a mixture of *E*-stilbene and *trans*-stilbene oxide. Conversion was estimated by integration of the peaks in the ^{1}H NMR spectrum from the CH= protons of the alkene at 7.07ppm and the CHO protons of the epoxide at 3.83ppm. Flash chromatography (1% ether - petrol) gave *trans*-stilbene oxide [20] (110 mg, 89%).

In control experiments, replacing the iminium salt in the above reaction with pyrrolidine triflate (13.9 mg, 0.063 mmol **or** 139 mg, 0.63 mmol) resulted in no epoxidation of *E*-stilbene being observed. Similarly, no epoxidation was observed when the iminium salt in the above procedure was replaced with 0.63 mmol of *o*-chlorobenzaldehyde, *o*-chloroacetophenone, or α-acetoxyacetone.

The product epoxides derived from *E*-stilbene [20], *E*-α-methylstilbene [21], 1-phenylcyclohexene [22], limonene [23], styrene [24], *Z*-stilbene [25], 2-cyclohexenol [5], *E*-chalcone [26], and *E*-ethylcinnamate [27] are all literature compounds.

The enantiomeric excess of epoxide products was determined by ^{1}H NMR in the presence of chiral shift reagents, as described by Yang [2].

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