Sustainable Epoxidation of Electron-Poor Olefins with Hydrogen Peroxide in Ionic Liquids and Recovery of the Products with Supercritical CO_2

Olga Bortolini,*[a] Sandro Campestrini,[b] Valeria Conte,*[c] Giancarlo Fantin,[a]
Marco Fogagnolo,[a] and Silvia Maietti[a]

Keywords: Epoxidation / Green chemistry / Ionic liquids / Peroxides / Supercritical fluids

An efficient procedure is described for the epoxidation of electron-deficient olefins, in particular Vitamin K_3 and analogues, with aqueous basic solutions of hydrogen peroxide in different ambient temperature ionic liquids (ILs) $[bmim^+][X^-]$ $\{[bmim^+]$ = 1-butyl-3-methylimidazolium; $[X^-] = [BF_4^-]$, $[CF_3SO_3^-]$, $[PF_6^-]$, $[N(CF_3SO_2)_2^-]\}$. Various factors affecting epoxide yield (in the range 80–99%), reaction rate and reproducibility have been examined. The almost quantitative extraction of the epoxides from the reaction media has been obtained with supercritical CO_2. The ionic liquid was then recovered and reused in subsequent cycles.

Introduction

Room temperature ionic liquids (ILs) are salts, characterised by a low melting point and a wide liquidus range, that possess distinctive physical properties such as non-volatility, non-flammability and thermal stability. In addition, the presence of poorly coordinating ions and the ability to dissolve a wide range of organic and/or inorganic derivatives are salient features of these materials.[1−3] Because of their peculiar properties ILs have been proposed as solvents in environmentally benign processes. Selected examples include hydrogenation,[4] hydroformylation,[5] dimerisation and oligomerisation of alkenes,[6] Heck C−C coupling,[7] Friedel−Crafts reactions,[8] Diels−Alder cycloadditions,[9] selective and asymmetric epoxidations,[10,11] oxidations,[12] halogenations of double and triple bonds,[13] and biocatalytic processes.[14] In most of these reactions ionic liquids appear to be a good alternative to conventional organic solvents, providing comparable or higher rates and, in some cases, improved enantioselectivities.

Hydrogen peroxide is a clean, cheap and potentially powerful oxygen-transfer reagent that has recently regained importance both in the industrial and academic communities.[15] The two main reasons are: from the one side, H_2O_2 is nowadays employed in the chemical industry in a safer, more efficient and innovative mode, and from the other hydrogen peroxide is a clean oxidant with limited waste problems as its reduction product is water.[15]

The use of hydrogen peroxide in ionic liquids for the oxidation of organic derivatives is still at an early stage. The few reported examples include the oxidation of several unfunctionalised alkenes with a urea−hydrogen peroxide adduct or hydrogen peroxide in the presence of methyltrioxorhenium,[11,16] the epoxidation of simple olefins by the H_2O_2/Fe^{III} porphyrin system under biphasic conditions,[17] the selective oxidation of styrene to acetophenone with H_2O_2 mediated by palladium chloride,[12] and the epoxidation of cyclohexene by peroxyoctanoic acid generated in situ by the immobilized *Candida antarctica* catalysed reaction of octanoic acid with 60% aqueous H_2O_2.[18]

Carbon dioxide in the supercritical state is used to replace hazardous halogenated and aromatic solvents for extractions, separations and as a reaction medium in industry.[19] The characteristics which make carbon dioxide an attractive substance from an environmental point of view are its chemical inertness, non-flammability and non-toxicity. In spite of the fact that carbon dioxide is a "greenhouse gas" its uses can be considered environmentally benign if carbon dioxide is recycled so that there is no net increase in the atmosphere.

We recently reported an efficient methodology for the epoxidation of α ,β -unsaturated ketones using basic aqueous solutions of hydrogen peroxide, a transformation known as the Weitz−Scheffer reaction, in ionic liquids.[10]

---

[a] Dipartimento di Chimica, Università di Ferrara,
Via Borsari 46, 44100 Ferrara, Italy
Fax: (internat.) +39-0532-240-709
E-mail: brl@unife.it
[b] Dipartimento di Chimica Organica, Università di Padova,
Via Marzolo 1, 35131 Padova, Italy
Fax: (internat.) +39-049-827-5239
E-mail: sandro.campestrini@unipd.it
[c] Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata,
Via della ricerca Scientifica, 00133 Roma, Italy
Fax: (internat.) +39-06-7259-4328
E-mail: valeria.conte@uniroma2.it

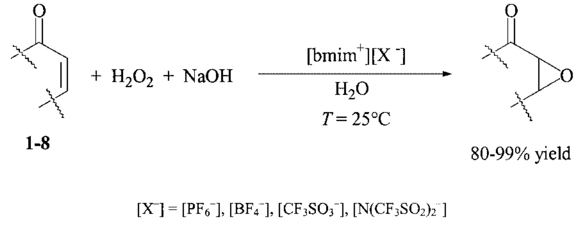
DOI: 10.1002/ejoc.200300442

In this paper we examine some of the factors that control the reactivity by: i) expanding the number of ionic liquids employed, ii) optimising the oxidation conditions in terms of the relative substrate-base-H_2O_2 ratio, and iii) finding the most favourable conditions for epoxide extraction using supercritical CO_2 followed by the recovery and reuse of the ionic liquid.[20] This investigation has been extended applying the oxidation protocol to other substrates, especially models closely related to the Vitamin K class that are prothrombogenic and antihemorrhagic derivatives.[21] The vitamin K epoxides are also very important because of their higher light stability as compared to the non-oxidised derivatives.

Results and Discussion

Epoxidation reactions were carried out at room temperature utilising 1-butyl-3-methylimidazolium·$[X^-]$ ($[bmim^+][X^-]$) as solvents. $[bmim^+][BF_4^-]$ and $[bmim^+][CF_3SO_3^-]$ are hydrophilic ILs, whereas $[bmim^+][PF_6^-]$ and $[bmim^+][N(CF_3SO_2)_2^-]$ are only partially miscible in water. These ILs were chosen on the basis of their stability and availability.

A typical reaction, exemplified in Scheme 1, is carried out at 25 °C by dissolving 1 mmol of the substrate in 1 mL of the IL. To this mixture, kept under vigorous stirring, 4 mmol of water, 2 mmol of solid NaOH, and 3 mmol of H_2O_2 (0.3 mL of commercially available aqueous solution 30% w/w) were subsequently added. The extent of the reaction was monitored by GC analysis (see Exp. Sect. for details). Chromatographic, and in some cases ^1H NMR, comparison with genuine epoxides, obtained in the classical reaction carried out with H_2O_2/HO^- in water, was used to identify the products.[22]



Scheme 1

In our previous communication[10] we reported data related to some substrates and with two ILs — $[bmim^+][BF_4^-]$ and $[bmim^+][PF_6^-]$. Subsequently, a discussion in the literature was opened concerning the reproducibility of product yields and reaction rates using different batches of ILs.[23] In our case, we observed that the oxidation reactions performed in the same batch of ionic liquid give consistent results in terms of both reaction rate and yield. Similar yields with different — in some cases very different — reaction times are observed for the same substrate in various batches of $[bmim^+][PF_6^-]$, including commercially available samples. As an example, the quantitative epoxidation of 2-cyclohexen-1-one in the IL used in the communication[10] is obtained in a few minutes, whereas three and five hours are required to complete the oxidation using the IL obtained from two distinct preparations. Furthermore, no reaction was observed using an as-received commercial sample of $[bmim^+][PF_6^-]$. The absence of reactivity could be attributed, in this case, to a high acid content in the IL. In fact, quantitative olefin conversion was completely restored upon treatment to neutral pH, with a final epoxide yield of 98%, although in a few hours. The presence of water in the medium is an additional problem that has been encountered with $[bmim^+][PF_6^-]$. Despite the reported low miscibility of water with this ionic liquid, we have observed a significant increase of epoxidation rates and reproducibility after addition of small quantities of H_2O to the solvent. Examples of this effect, using 3,5-dimethyl-2-cyclohexen-1-one, are given in Table 1.

Table 1. Effect of the presence of water on the epoxidation rates of 3,5-dimethyl-2-cyclohexen-1-one, with H_2O_2/OH^- in $[bmim^+][PF_6^-]$ as IL

Solvent[a]	Time (min)	Epoxide yield (%)
IL batch A	300	99
IL batch A + H_2O[b]	90	99
IL batch B	240	98
IL batch B + H_2O[b]	90	97

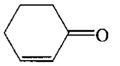
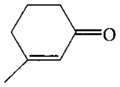
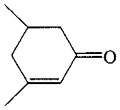
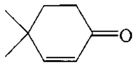
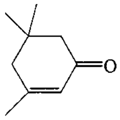
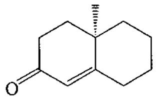
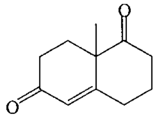
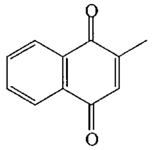
[a] Batch A and B refer to two different IL preparations. NB Several preparations of common ionic liquids like *N,N′*-dialkylimidazolium salt derivatives are now available, including solvent-free routes.[24] We therefore prepared two different batches of $[bmim^+][PF_6^-]$ to be used in the oxidation reactions. [b] H_2O ca. 4 mmol.

It may be inferred that the addition of water causes a "saturation" of the IL, which buffers the medium and allows a more reproducible system as far as solubility and solvation of the reagents is concerned. Taking into account these findings we have observed a considerable reduction of the discrepancies described above by following the synthetic protocol described in the Exp. Sect. mainly related to the preparation of $[bmim^+][PF_6^-]$, by adding small amounts of water to the reaction medium and by checking, before use, all new ILs by a standard reaction. All these precautions have therefore been used to obtain all the reactivity data reported in the tables. For uniformity, we also carried out all the reactions in the presence of water.

The relevant results related to the epoxidation of alkenes **1**−**8** as a function of the ionic liquid, in the optimised oxidation conditions indicated above, are reported in Table 2.

Inspection of the data of Table 2 shows that the best results in terms of product yield and reaction rate with all substrates were obtained with $[bmim^+][CF_3SO_3^-]$. A significant example refers to the methyl-substituted 1,4-naphthoquinone **8** (Vitamin K_3), which is almost quantitatively

Table 2. Base-catalysed oxidation of selected electrophilic alkenes with H_2O_2 in ionic liquids as a function of the different [X^-] counterions

Alkene	Epoxide yield, % (time, min)[a]			
	[BF_4^-]	[$CF_3SO_3^-$]	[PF_6^-]	[$N(CF_3SO_2)_2^-$]
 **1**	98 (5)	99 (5)	98 (5)	99 (5)
 **2**	97 (5)	99 (5)	99 (30)	84 (5) 99 (30)
 **3**	[b]	97 (30)	25 (30) 99 (90)	22 (30) 47 (90)
 **4**	[b]	99 (30)	20 (30) 85 (120)	2 (30)
 **5**	traces (120)	80 (120)	traces (120)	41 (120)
 **6**	[b]	40 (30) 81 (300)	6 (30) 15 (300)	7 (300)
 **7**	99 (5)	99 (1)	99 (5)	99 (1)
 **8**	[b]	99 (1)	99 (60)	99 (60)

[a] [substrate]:[H_2O_2]:[OH^-] = 1:3:2, 4 mmols of water were added to all the reaction mixtures. [b] These reactions were not performed because of the observed low stability of [$bmim^+$][BF_4^-] at longer reaction times.

converted into the corresponding epoxide in minutes depending on the solvent. The same substrate is oxidized over much longer reaction times[25,26] in various experimental conditions (from two hours up to four days). Our oxidation procedure also appears to be efficient with other ILs, like [$bmim^+$][PF_6^-], the reaction rates being higher than those observed in the conventional alkaline-aqueous conditions.[22–27] As a further comment we would like to point out that with the classical alkaline-aqueous conditions side reactions that strongly influence the isolated yields of epoxides are often observed.[28] Such a problem has never been observed in our experimental conditions.

Comparison of the results obtained with structurally similar substrates appears to suggest that a significant interaction between the substrate and the solvent is occurring. Such an effect is particularly evident with **6** (81% epoxide yield in 300 min) and **7** (99% epoxide yield in 5 min). Differences in the preferred conformation of the substrate or hydrogen-bond interactions of the substrates with the solvents are probably playing a role in determining the observed discrepancies. This point is currently under investigation with the aid of computational calculations.

A study dedicated to the optimisation of the oxidation protocol aimed at obtaining a more appealing procedure was then performed. To this aim 2-cyclohexen-1-one (**1**) was used as model substrate and [$bmim^+$][$CF_3SO_3^-$] or [$bmim^+$][PF_6^-] as solvent. The relevant results are shown in Table 3.

Table 3. Base-catalysed oxidation of 2-cyclohexen-1-one (**1**) with H_2O_2 in ionic liquids

Entry	H_2O_2 (equiv.)	OH^- (equiv.)	Time (min)	Epoxide yield (%)
		[$bmim^+$][$CF_3SO_3^-$]		
1	3	2	5	99
2	3	0.5	5	99
3	3	0	1200	traces
4	1.5	0.5	5	85
		[$bmim^+$][PF_6^-]		
5	3	2	5	98
6	3	0.5	5	95
7	3	0	1200	80
8	1.5	0.5	5	90

As the first step of this optimisation we reduced the amount of base from 2 to 0.5 equivalents with no significant reduction of the substrate conversion, which is complete in minutes at room temperature (entries 2 and 6). Under these conditions, halving the amount of hydrogen peroxide gives rise to a decrease of the epoxide yield from almost quantitative to 85% and 90%, respectively. It is worthwhile to note that the uncatalysed oxidation proceeds at a much slower rate in both ionic liquids (entries 3 and 7). With all substrates, however, a reduction of the base content to 0.5 equivalents causes insignificant differences in product yields and reaction times provided that three equivalents of H_2O_2 are used.

As reported by many authors, the classical epoxidation of α ,β -unsaturated carbonyl compounds using hydrogen peroxide in a basic medium suffer some drawbacks, so that several new methods have been proposed in recent years.[29–31] In almost all cases, however, consistent differences are found between the reaction yield, as obtained by GC for example, and the isolated product yield. These differences are usually attributed to the difficulty of recovering the epoxide.

As the final part of this study we checked the viability of the extraction of the epoxides formed with $scCO_2$, with the aim of obtaining an even "greener" procedure for the epoxidation of our electrophilic alkenes. To this purpose we carried out some epoxidation reactions of 2-cyclohexen-1-one (**1**), using the optimised reaction conditions as far as the molar ratio of reagents is concerned, save for having a different total volume of IL ([$bmim^+$][PF_6^-]) solvent. In particular, three different reactions were carried out reducing the total amount of IL used from 0.50 mL, down to

0.25 mL and 0.10 mL. The reaction mixtures were left to react, in a suitable glass vessel, for about one hour in order to assure a quantitative substrate conversion. Subsequently, after the addition of the appropriate amount of a chromatographic standard completely soluble in the $scCO_2$ phase (*n*-decane), the vessel was inserted into a dedicated steel reactor with an internal volume of 8.5 mL and pressurised with CO_2 until the final conditions of 40 °C and 200 atm. Under these experimental conditions, CO_2 is in the supercritical state and shows a density of 0.84 g/mL — very close to that of a saturated hydrocarbon; it therefore exhibits a similar solvent power. After a contact time of about 19 hours, the amount of epoxide extracted into the $scCO_2$ was determined through the withdrawal and GC analysis of supercritical-phase samples (see Exp. Sect. for details).

The data collected in Table 4 confirm that all the reactions are characterised by a very high degree of substrate conversion independent of the counteranion present in the solvent. On the other hand, as the total volume of the reactor is constant, the efficiency of the extraction procedure increases as the volume of the reaction mixture decreases. The data also indicate that the epoxide solubility is scarcely influenced by the nature of the IL counterion. Moreover, in the case of $[N(CF_3SO_2)_2^-]$ the possibility of a reversible reaction with CO_2 that changes the counterion into a carbamate-like one should be taken into account.

Table 4. Conversion of substrate and efficiency of the extraction with $scCO_2$ of cyclohexanone-2-epoxide formed by the reaction of 2-cyclohexen-1-one (**1**) with H_2O_2 in the presence of NaOH in various $[bmim^+][X^-]$[a]

Run	React. volume (mL)	Conversion (%)	$[X^-]$	Epoxide extraction (%)
1	0.50	97	$[PF_6^-]$	66
2	0.25	97	$[PF_6^-]$	71
3	0.10	>99	$[PF_6^-]$	96
4	0.10	>99	$[CF_3SO_3^-]$	94
5	0.10	>99	$[N(CF_3SO_2)_2^-]$	92

[a] $[1]:[H_2O_2]:[NaOH] = 1:1.5:0.5$.

Once we had verified the complete solubility of *n*-decane in the supercritical phase under all the experimental conditions of Table 4, the above reported data allowed us to estimate the solubility of cyclohexanone-2-epoxide in $scCO_2$ (40 °C, 200 atm). In fact, run 1 of Table 4 indicates that 66% of the initial amount of 2-cyclohexen-1-one (50 mg) was extracted as cyclohexanone-2-epoxide in 8.5 mL of a supercritical phase volume, leading to a solubility of ca. 3.9 mg/mL. Runs 2 and 3 in Table 4 show that upon decreasing the total amount of reaction mixture, and consequently decreasing the amount of reactants and standard, the extraction efficiency increases, passing from 66 to 71 up to 96% but, at the same time, epoxide solubility in the supercritical phase decreases. For instance, run 3 of Table 4 shows that 96% of the starting 2-cyclohexen-1-one (10 mg) was extracted as the corresponding epoxide, leading to a solubility of ca. 1.1 mg/mL. This outcome is probably related to a change of $scCO_2$ solvent power induced by the standard (*n*-decane), which acts as a solvent modifier. Incidentally, these results suggest a possible method to improve epoxide solubility in industrial applications exploiting batch reactors. Alternatively, efficient epoxide extractions may be obtained even in the case of very low solubilities by taking advantage of continuous flow reactors, in which a stream of $scCO_2$ is employed and recycled after an expansion step, which allows the separation of the epoxide. With these results at hand it is possible to underline that the coupling of the use of IL liquids as solvents, hydrogen peroxide as oxidant and extraction of products with $scCO_2$ is a viable and sustainable procedure for the epoxidation of electron-poor olefins.

As a further improvement of our procedure, the possibility of performing subsequent cycles of reaction/$scCO_2$ extraction of products by reusing the IL solvent was explored. To this end, two series of reactions, whose results are collated in Table 5, were carried out by using the experimental conditions of run 3 in Table 4.

Table 5. Recycling of the solvent in the epoxidation of 2-cyclohexen-1-one (**1**) in $[bmim^+][PF_6^-]$ with H_2O_2 in the presence of NaOH

Cycles	Steel reactor		Glass reactor	
	Conv. (%)	Extrac. yield (%)	Conv. (%)	Extrac. yield (%)
1	82	79	97	99
2	78	90	91	89
3	35	>99	46	91
4[a]			>98	78

[a] IL washed with water before being recycled in order to eliminate Na_2CO_3 formed after extraction of the basic reaction mixture with $scCO_2$.

In the first series the subsequent reactions were carried out directly in the steel reactor illustrated in the Exp. Sect. In the second series, the reactions were carried out in a glass vessel which, after completion of oxidation, was introduced into the steel vessel for $scCO_2$ extraction; details are reported in the Exp. Sect.

As far as the utilisation of the steel reactor as reaction vessel is concerned, it is worthwhile to note that the substrate conversions are lower than those observed for reactions carried out in the glass vessel. This is probably related to a surface metal catalysed radical decomposition of the oxidant as observed previously.[32] This observation thus illustrates one of the problems that have to be taken into consideration if this oxidation procedure is to be used. The further decrease of substrate conversion observed after recycling the IL is probably a consequence of NaOH neutralisation by CO_2 during the extraction step, with the formation of Na_2CO_3. Another unsatisfactory feature of the reactions carried out in the steel vessel is the non-quantitative recovery of organic materials by $scCO_2$ extraction. A possible rationale for this is the formation of highly polar products, in particular diols, which are not extracted into $scCO_2$

under the experimental conditions selected. Conversely, in the reactions carried out in the glass reactor, the decomposition of the peroxide does not take place and therefore in the first cycle we observe the expected high conversion of the substrate and high yield (almost quantitative) of epoxide extraction. However, in the second cycle, a decrease in the conversion due to Na_2CO_3 precipitation during the extraction step is detectable (91% vs. 97%). An even more marked decrease in conversion (46%) was observed during the third cycle.

At this stage the IL was washed with water to eliminate Na_2CO_3, and dried before being reused in a fourth cycle where hydrogen peroxide and base were reloaded. The conversion and extraction yield thus obtained were again very good.

Conclusion

The oxidation procedure outlined in this paper is characterised by a number of advantages that make it a very interesting environmentally friendly process for the base-catalysed oxidation of electrophilic alkenes. In particular, we have reported a successful combination of new and less-threatening solvents {i.e. $[bmim^+][X^-]$ with $[X^-] = [PF_6^-]$, $[CF_3SO_3^-]$, $[N(CF_3SO_2)_2^-]$}, H_2O_2 — one of the safer, least wasteful and cheaper oxidants — and an efficient, clean and safe extraction of the products with $scCO_2$. Worthy of note is the fact that complete consumption of the substrates is usually observed, in short reaction times, in the presence of small excesses of the oxidant and a submolar quantity of the base at room temperature. The efficiency of the extraction with $scCO_2$ is almost quantitative as well. We have also showed that recovery and reuse of the ionic liquid is achievable.

The use of ILs in the base-catalysed epoxidation of electron-poor olefins appears also to be of interest for the enantioselective versions of such reaction.[25,26,33]

Experimental Section

Instruments: GC analyses were performed on a FISONS GC 9000 series, using a DETTBS column (Mega). ^1H NMR spectra were recorded on a Varian Gemini 300 MHz. Thermostatted liquid circulation was obtained using a Haake GH refrigerator controlled by a Haake D8 head. Extraction of epoxides with $scCO_2$ was performed on a modified SFC 3000 series Carlo−Erba instruments originally designed for capillary supercritical fluid chromatography.

General Procedure for the Epoxidation of Alkenes: In a typical reaction 1 mmol of the substrate was dissolved in 1 mL of 1-butyl-3-methylimidazolium hexafluorophosphate $[bmim^+][PF_6^-]$ at 25 °C in a 5 mL volumetric flask. Water (4 mmol), 2 mmol of solid NaOH, and 0.3 mL of commercially available aqueous solution of H_2O_2 (30% w/w) 3 mmol were then added with vigorous stirring. At increasing reaction times, samples of the mixture were taken out, poured into water (1 mL), extracted with ethyl acetate, dried over $MgSO_4$ and analysed by GC. No changes were observed when NaOH was dissolved in aqueous hydrogen peroxide before addition to the reaction mixture. The identity of the epoxides was determined on products isolated from reactions carried out on a larger scale by comparison of the ^1H NMR spectra with those obtained for genuine epoxides prepared using the classical H_2O_2/HO^- reaction.[22−28]

General Procedure for Extraction of Epoxides with $scCO_2$: An amount of *n*-decane (internal standard) depending on the volume of reaction mixture employed was added to the mixtures obtained after reaction either in a glass vessel or directly in the steel vessel under the experimental conditions of Table 3 and 4, and the product was extracted through an overnight exposure to $scCO_2$ by using the apparatus shown in Figure 1. The system core is a modified SFC 3000 series Carlo−Erba Instrument originally designed for capillary supercritical fluid chromatography. The capillary column and splitting valve were replaced by a 316 stainless steel 8.5-mL high-pressure vessel (10000 psig) connected to a restrictor (1/16" OD, 0.005" ID) through a six-way HPLC valve (Rheodyne 7125) for withdrawing reaction samples. The apparatus consists of a SFC 300 Carlo−Erba Instruments pump, a chromatographic SFC 3000 Carlo−Erba Instruments oven containing the reaction vessel and an ICU 600 from Carlo−Erba Instruments for the temperature control of the oven and restrictor. The SFC 300 is a 150 mL capacity pulse-free syringe pump developed for pressures ranging up to 50 MPa and flow rates from 1 to 7000 μL/min. The pump cylinder is thermostatted at 7 °C by an external liquid circulation thermostat thus permitting the syringe to be easily refilled with liquid carbon dioxide. A sample of the supercritical phase was withdrawn through the stainless steel restrictor maintained at 80 °C, by means of a six-way HPLC valve and trapped in dichloromethane. The extraction yield and conversions were then determined by GLC analysis with the internal standard method on the basis of previously measured response factors.

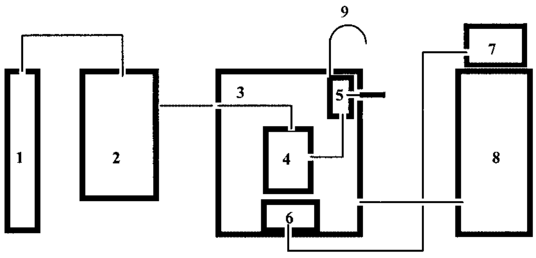


Figure 1. Home made apparatus for extraction with $scCO_2$; 1: CO_2 reservoir; 2: cryogenic pump (Carlo−Erba SFC 300); 3: thermostatic oven (Carlo−Erba SFC 3000); 4: reactor; 5: six-way valve; 6: alternating field magnetic stirrer; 7: magnetic stirrer control unit; 8: restrictor and oven temperature control unit (Carlo−Erba ICU 600); 9: restrictor

Preparation of $[bmim^+][PF_6^-]$: 1-Butyl-3-methylimidazolium chloride was prepared by reaction of 1-methylimidazole (ca. 10 g) with chlorobutane (60 mL) under reflux for 24 hours. The disappearance of 1-methylimidazole was followed by TLC using $CHCl_3/CH_3OH/NH_4OH$ (90:15:1) as eluent. The excess of chlorobutane was removed by evaporation under vacuum. To prepare $[bmim^+][PF_6^-]$, 1-butyl-3-methylimidazolium chloride (5 g) was dissolved in 70 mL of water, the solution was cooled in an ice-cold bath, and hexafluorophosphoric acid (1.3 equivalents) was slowly added over a period of 2 hours. After stirring for 12 hours and warming to room temperature, the upper acidic aqueous layer was decanted and the lower ionic-liquid portion was washed with water to neutral pH. The ionic liquid was then heated under vacuum at 70 °C to remove any excess water.[34] All new batches of $[\mathrm{bmim}^+][\mathrm{PF}_6^-]$ were checked in a standard reaction before use. The synthesis of $[\mathrm{bmim}^+][\mathrm{X}^-]$ {X = $[\mathrm{BF}_4^-]$,[35] $[\mathrm{CF}_3\mathrm{SO}_3^-]$[36] and $[\mathrm{N}(\mathrm{CF}_3\mathrm{SO}_2)_2^-]$[36]} was performed according to literature methods.

Acknowledgments

We acknowledge financial support from the Italian Ministry of University and Scientific and Technological Research to the project: "Activation of Peroxidic Species in Innovative Selective Oxidation Processes". We wish to thank Prof. K. R. Seddon for helpful discussions and for a generous gift of ILs.

---

[1] T. Welton, *Chem. Rev.* **1999**, *99*, 2071−2083.
[2] P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926−3945; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772−3789.
[3] R. A. Sheldon, *Chem. Commun.* **2001**, 2399−2407.
[4] Y. Chauvin, L. Mussmann, H. Oliver, *Angew. Chem.* **1995**, *107*, 2941−2943; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2698−2700.
[5] E. G. Kuntz, *CHEMTECH* **1987**, 570−576.
[6] J. E. L. Dullius, P. A. Z. Suarez, S. Einloft, R. F. de Souza, J. Dupont, J. Fisher, A. De Cian, *Organometallics* **1998**, *17*, 815−819.
[7] A. J. Carmichael, M. J. Earle, J. D. Holbrey, P. B. McCormac, K. R. Seddon, *Org. Lett.* **1999**, *1*, 997−1000.
[8] J. A. Boon, J. A. Levisky, J. L. Pflug, J. S. Wilkes, *J. Org. Chem.* **1986**, *51*, 480−483.
[9] J. Howarth, K. Hanlon, D. Fayne, P. McCormac, *Tetrahedron Lett.* **1997**, *38*, 3097−3100.
[10] O. Bortolini, V. Conte, C. Chiappe, G. Fantin, M. Fogagnolo, S. Maietti, *Green Chem.* **2002**, *4*, 94−96.
[11] S. Owens, M. M. Abu-Omar, *Chem. Commun.* **2000**, 1165−1166.
[12] V. V. Namboodiri, R. S. Varma, E. Sahle-Demessie, U. R. Pillai, *Green Chem.* **2002**, *4*, 170−173.
[13] O. Bortolini, M. Bottai, C. Chiappe, V. Conte, D. Pieraccini, *Green Chem.* **2002**, *4*, 621−627.
[14] R. A. Sheldon, R. Madeira Lau, M. J. Sorgedrager, F. van Rantwijk, K. R. Seddon, *Green Chem.* **2002**, *4*, 147−151.
[15] C. W. Jones, *Application of Hydrogen Peroxide Derivatives*, RSC London, 1999.
[16] G. S. Owens, A. Durazo, M. M. Abu-Omar, *Chem. Eur. J.* **2002**, *8*, 3053−3059.
[17] K. A. Srinivas, A. Kumar, S. M. S. Chauhan, *Chem. Commun.* **2002**, 2456−2457.
[18] R. Madeira Lau, F. van Rantwijk, K. R. Seddon, R. A. Sheldon, *Org. Lett.* **2000**, *2*, 4189−4191.
[19] *Supercritical Fluids, Extraction and Pollution Prevention* (Eds.: M. A. Abrahm, A. K. Sunol), ACS Symposium series, vol. 670, American Chemical Society, Washington, DC, 1997.
[20] S. V. Dzyuba, R. A. Bartsch, *Angew. Chem.* **2003**, *115*, 158−160, *Angew. Chem. Int. Ed.* **2003**, *42*, 148−150, and refs. cited therein.
[21] P. Dowd, R. Hershline, S. W. Ham, S. Naganathan, *Nat. Prod. Rep.* **1994**, *11*, 251−264.
[22] *Org. Synth. Coll. Vol.* **1963**, *4*, 552−553.
[23] V. Farmer, T. Welton, *Green Chem.* **2002**, *4*, 97−102.
[24] J. H. Davis Jr., K. J. Forrester, T. Merrigan, *Tetrahedron Lett.* **1998**, *39*, 8955−8958.
[25] S. Colonna, A. Manfredi, R. Annunziata, N. Gaggero, *J. Org. Chem.* **1990**, *55*, 5862−5866.
[26] S. Arai, H. Tsuge, M. Oku, M. Miura, T. Shioiri, *Tetrahedron* **2002**, *58*, 1623−1630.
[27] For a recent paper, see: K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Org. Chem.* **2000**, *65*, 6897−6903 and references cited therein.
[28] See the Exp. Sect. of: J. Eling, H. Lempers, R. A. Sheldon, *Eur. J. Org. Chem.* **2000**, 1905−1911.
[29] J. M. Fraile, J. I. Garcia, C. Cativiela, J. A. Mayoral, F. Figueras, *Tetrahedron Lett.* **1996**, *37*, 5995−5996.
[30] T. S Straub, *Tetrahedron Lett.* **1995**, *36*, 663−664.
[31] A. Sharifi, M. Bolourtchian, F. Mohsenzadeh, *J. Chem. Res. (S)* **1998**, 668−669.
[32] S. Campestrini, U. Tonellato, *Adv. Synth. Catal.* **2001**, *343*, 819−825.
[33] M. W. Cappi, W. P. Chen, R. W. Flood, Y. W. Liao, S. M. Roberts, J. Skidmore, J. A. Smith, N. M. Williamson, *Chem. Commun.* **1998**, 1159−1160.
[34] J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser, R. D. Rogers, *Chem. Commun.* **1998**, 1765−1766.
[35] P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. De Souza, J. Dupont, *Polyhedron* **1996**, *15*, 1217−1219.
[36] P. Bonhote, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.* **1996**, *35*, 1168−1178.

Received July 16, 2003