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# Sustainable cyclic carbonate production, utilising carbon dioxide and azolate ionic liquids

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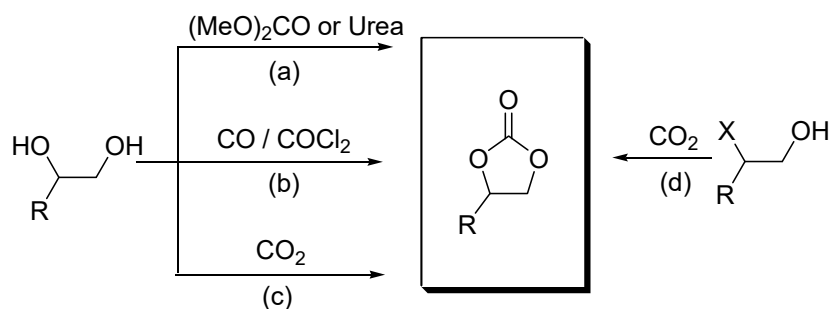
**Abstract:**

An efficient protocol is described for producing cyclic carbonates in good to excellent yields under moderate reaction conditions (100.0 °C, 1.0 MPa) by treating epoxides with carbon dioxide, promoted by a series of azolate ionic liquids, which are effective recyclable metal-free and halide-free catalysts.

**Keywords:** Green chemistry, azolate ionic liquids, recyclable catalysts, epoxides, cyclic carbonates.

**INTRODUCTION**

Carbon dioxide is a greenhouse gas thought to be involved in global warming and climate change.<sup>1,2</sup> Nevertheless, it offers a virtually inexhaustible, inexpensive, non-flammable and readily available C1 feedstock for organochemical processes.<sup>3-7</sup> The direct conversion of CO<sub>2</sub> to five- or six-membered cyclic carbonates<sup>8-10</sup> is one of the most promising strategies for producing highly desirable solvents for electrolytes in Li-ion rechargeable batteries.<sup>11,12</sup> Cyclic carbonates are also utilised as monomers in polymerisation reactions,<sup>13,14</sup> as intermediates in the synthesis of fine chemicals<sup>7</sup> and as high boiling aprotic polar solvents.<sup>15-17</sup> There have been many varied reports of synthetic routes to yield cyclic carbonates, and the most important of these are summarised in Scheme 1. In addition, Lewis acidic catalysts including SnCl<sub>4</sub><sup>18</sup>, cobalt porphyrin<sup>19</sup> and chromium / zinc / aluminum salen<sup>20, 21</sup> have also been reported to catalyze this cycloaddition reaction. However, most of these catalyst systems need bases or tetraalkylammonium halides as co-catalysts; and in some cases, either the use of expensive reagents or harsh reaction conditions were required for an efficient reaction.<sup>22-33</sup>



Entry	Substrate	“CO” Source	Catalyst system	Conditions	Yield / %	Ref
1	1,2-diols	Urea	FeBr <sub>2</sub>	150.0 °C, 18.0 h, 1,4-dioxane	92.0	22
2	1,2-diols	(MeO) <sub>2</sub> CO	NHC <sup>a</sup>	74.0 °C, 6.0 h	58.0	23
3	1,2-diols	CO	Pd/C, KI, O <sub>2</sub> , Na[O <sub>2</sub> CMe]	100.0 °C, 3.0 h, 1.5 MPa, MeOCH <sub>2</sub> CH <sub>2</sub> OMe	91.0	24-26
4	1,2-diols	CO <sub>2</sub>	NHC <sup>a</sup> /Base/RX	90.0 °C, 24.0 h, 0.1 MPa	81.0	28
5	Haloalcohol	CO <sub>2</sub>	Basic ionic liquids	25.0 °C, 14.0 h, 1.0 MPa	90.0	29
6	Haloalcohol	CO <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	40.0 °C, DMF, 0.1 MPa	75.0	30

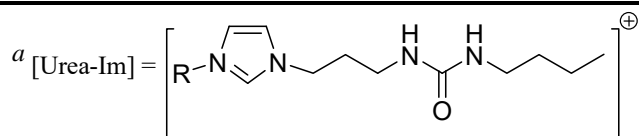
<sup>a</sup> NHC= *N*-heterocyclic carbene

**Scheme 1.** Synthesis of cyclic carbonates from organic precursors.

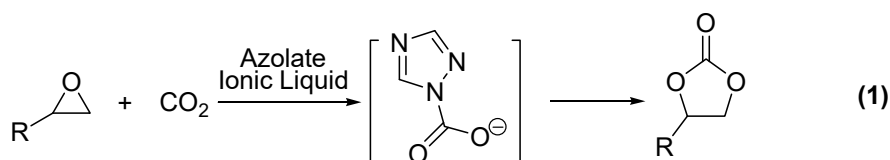
Ionic liquids<sup>34</sup> have been used for the synthesis of a myriad of organic chemicals.<sup>35</sup> Of specific interest here, there have been number of attempts to use ionic liquids to make cyclic carbonates.<sup>36-42</sup> Some key processes, to date, using homogenous ionic liquid systems are summarised in Table 1. It is noteworthy, that there have also been a number of solid-supported ionic liquid systems<sup>41-46</sup> employed for producing cyclic carbonates. Though they produce high yields of products, these systems also contain undesirable halides and/or metals.

Table 1. Halide ionic liquids catalysed cycloaddition reactions of epoxides and CO<sub>2</sub>.

Entry	Epoxide	IL	Conditions	Yield %	ref
1	Styrene oxide	[ArPPh <sub>3</sub> ]Br	60.0 °C, 24.0 h, 0.1 MPa	91.0	36
2	Propylene oxide	[(mim) <sub>2</sub> Zn]Br <sub>2</sub>	120.0 °C, 4.0 h, 0.5 MPa	78.0	37
3	Propylene oxide	[Urea-Im]I <sup>a</sup>	130.0 °C, 3.0 h, 1.0 MPa	97.0	38
4	Propylene oxide	[(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> NH]I	110.0 °C, 6.0 h, 2.0 MPa	91.0	39
5	Epichlorohydrin	[bim-ArOH]Br	120.0 °C, 1.0 h, 1.0 MPa	90.0	40

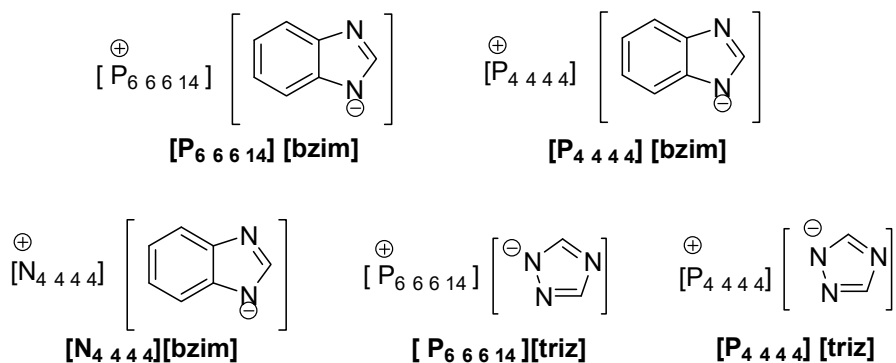


The work described in this paper, utilises ionic liquids with azolate anions, which in previous literature reports refer to as *superbasic ionic liquids*.<sup>47</sup> Even though they are more basic than common trialkylamines, the  $pK_a$  values of their conjugate acids would not warrant them to qualify as superbasic substances.<sup>48-50</sup> Nevertheless, their associated anions possess sufficiently high nucleophilicity to attach weakly electrophilic CO<sub>2</sub>, enabling them to be used in CO<sub>2</sub> gas capture and catalysis.<sup>47, 51-55</sup> In this paper, we refer to them as *azolate ionic liquids (or salts)*.



The key step (see equation 1) in this reaction is the formation of a reactive carbamate intermediate by nucleophilic addition of the azolate anion to CO<sub>2</sub>. This carbamate intermediate

also has been shown to react with other substrates, including propargylic alcohols, 2-aminobenzonitriles, 1,2-phenylenediamines, and 2-aminothiophenol, thereby producing  $\alpha$ -alkylidene cyclic carbonates,<sup>53</sup> or  $\alpha$ -hydroxy ketones,<sup>54</sup> quinazoline-2,4(1H,3H)-diones,<sup>55</sup> benzimidazolones,<sup>55</sup> and benzothiazoline,<sup>55</sup> respectively.



**Figure 1.** The azolate ionic liquids (or salts) used in this work.

Herein, we report a protocol involving metal- and halide-free azolate ionic liquid system for promoting the cycloaddition of CO<sub>2</sub> to epoxides to generate cyclic carbonates. These ionic liquids (or salts) contain benzimidazolate (bzim) or triazolate (triz) anions and trihexyltetradecylphosphonium (P<sub>66614</sub>), tetrabutylphosphonium (P<sub>4444</sub>) and tetrabutylammonium (N<sub>4444</sub>) cations (See Figure 1).

## EXPERIMENTAL SECTION

**Materials.** Benzimidazole (98.0%), 1,2,4-triazole (98.0%), tetrabutylammonium hydroxide (10.0% in methanol), propylene oxide (99.0%), styrene oxide (99.0%), 1,2-epoxyhexane (99.0%), 1,2-epoxypentane (99.0%), 1,2-epoxidodecane (99.0%), 1,2-epoxyoctane (99.0%) and cyclohexene oxide (99.0%) were purchased from Sigma-Aldrich and TCI. [P<sub>66614</sub>]Cl and [P<sub>4444</sub>]Cl were donated from Solvay-Cytec (98.0%). Gaseous carbon dioxide (99.9 %) was

obtained from BOC. Amberlite IRN-78 ion exchange resin was purchased from Alfa Aesar. All of the materials were used without further purification.

**Instruments.**  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were all recorded on a Bruker Ultrashield 400 plus spectrometer at 25.0 °C using dimethyl sulfoxide ( $\text{dms}\text{-}d_6$ ) or Chloroform ( $\text{CDCl}_3$ ) as solvent. ESMS-mass spectroscopy measurements were carried out on a Waters LCT Premier instrument with an Advion TriVersa NanoMate injection system (cone voltage 50 V, source 120.0 °C). Thermogravimetric analyses (TGA) were performed using a TGA/DSC thermogravimetric analyser from Mettler-Toledo, Inc. The samples were measured in alumina crucibles, at a heating rate of 5 K  $\text{min}^{-1}$  under a dinitrogen atmosphere. The onset of the weight loss in each thermogram was used as a measure of the decomposition temperature (the point at 5.0 wt% loss of the sample).

**Preparation of ionic liquids.**<sup>57, 58</sup> In a typical reaction,  $[\text{P}_{4444}]\text{Cl}$  (19.9 g, 67.5 mmol) was dissolved in absolute ethanol (25.0  $\text{cm}^3$ ) and passed through a column packed with at least three equivalents (in terms of the number of OH-exchange groups) of anion exchange resin (Amberlite IRN-78, OH-form, which had been prewashed with absolute ethanol to wet sufficiently and remove any air from the resin). The eluent was passed through the same column a further two times and then passed through a fresh column once more. The resultant ethanolic solution of  $[\text{P}_{4444}][\text{OH}]$  was tested for the absence of remaining halide ions, using standard acidification and treatment with silver(I) nitrate. The amount of  $[\text{P}_{4444}][\text{OH}]$  in its ethanol solution was then determined by  $^1\text{H}$  NMR. The necessary amount of benzimidazole (7.8 g, 66.1 mmol) was added into the solution and stirred for 24 h at room temperature. Solvent was removed *in vacuo* and the product was dried for at least 24 h under high vacuum ( $\sim 10^{-2}$  bar) at 60.0 °C, yielding the  $[\text{P}_{4444}][\text{bzim}]$  as a pale yellow viscous liquid. The other ionic liquids,  $[\text{P}_{66614}][\text{bzim}]$ <sup>56</sup>,

[P<sub>66614</sub>][triz]<sup>51</sup> and [P<sub>4444</sub>][triz]<sup>54</sup> were prepared by an analogous route. [N<sub>4444</sub>][bzim] was prepared as a white solid by mixing equimolar quantities of tetrabutylammonium hydroxide (10.0% in methanol) and benzimidazole.

**General experimental procedure for the cycloaddition reaction of CO<sub>2</sub> and epoxide.** All the reactions were carried out in a stainless-steel autoclave (16.0 cm<sup>3</sup>) equipped with an automatic stirrer (600 rpm) and temperature control system. The selected epoxide (5.0 mmol) and ionic liquid (0.25 mmol) were added into the autoclave successively. CO<sub>2</sub> (1.0 MPa) was charged in the reactor at ambient temperature. The reaction was carried out in the range 25-100 °C under autogenous conditions, for the appropriate time (up to 24 h) with continuous stirring. The autoclave was cooled to room temperature and then the excess of pressure was released, the product was analysed by <sup>1</sup>H NMR spectroscopy.

The detailed results of the reaction between propylene oxide and CO<sub>2</sub> are reported in Table 2, which led to the establishment of optimal conditions. The reactions of other epoxides were studied under these conditions, and these results are detailed in Table 3.

## RESULTS AND DISCUSSION

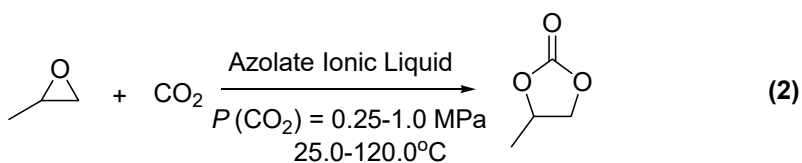
### Preparation of ionic liquids

Typically, tetraalkylphosphonium chloride was added to an excess of OH-anion exchange resin, to produce aqueous tetraalkylphosphonium hydroxide solutions, which were then neutralized by the addition of stoichiometric amounts of either a diazole or triazole.<sup>56-58</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy established both the purity and stoichiometry of the product ionic liquids, and the presence of anions and cations was confirmed by high resolution mass spectrometry. The characteristics of the prepared ionic liquids compared well with earlier literature reports.<sup>56-58</sup> All



the products were viscous pale yellow liquids, except [N<sub>4444</sub>][bzim], which was a white powder, and [P<sub>4444</sub>][bzim], which was an immobile glass.

**Reaction of propylene oxide with CO<sub>2</sub>** The reaction of propylene oxide with carbon dioxide was studied, in detail, under a wide variety of conditions, *viz* temperature, pressure, mol % of ionic liquids and reaction time (see Figure 2, 3 and Table 2). Under all conditions, only a single reaction product, propylene carbonate, was identified, as shown in Equation 2.

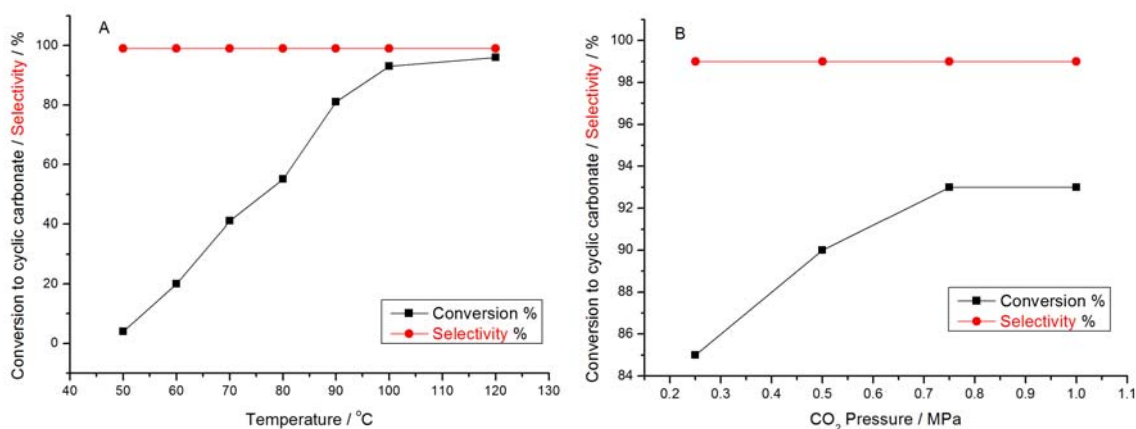


A series of experiments were performed in order to find the optimal conditions for the reaction above and then, these conditions were later used to study the reactions of a range of other epoxides (see Table 3).

In specific detail, when the reaction was conducted under ambient conditions using [P<sub>66614</sub>][bzim], only trace amounts of propylene carbonate were observed by NMR spectroscopy (Table 2, entry 2). When the reaction was carried out at 80.0 °C and 1.0 MPa CO<sub>2</sub> pressure, the product yield was elevated to 74.0% (Table 2, entry 3). In a blank experiment, no product was observed in the absence of azolate ionic liquids (Table 2, entry 1). For comparison, the other ionic liquids, including [P<sub>4444</sub>][bzim], [N<sub>4444</sub>][bzim], [P<sub>66614</sub>][triz], and [P<sub>4444</sub>][triz] were examined for this reaction, as well. The results indicated that [P<sub>4444</sub>][bzim] and [N<sub>4444</sub>][bzim] showed the highest reactivity compared with [P<sub>66614</sub>][bzim] (Table 2, entries 3, 4, 5). While [P<sub>4444</sub>][triz] exhibited lower activity than [P<sub>4444</sub>][bzim] (Table 2, entries 4, 7). The significant differences in the chemical structure of these azolate ionic liquids leading to different basicities of the associated anions ( $\text{p}K_{\text{a}}$  of benzimidazole = 16.4,<sup>54</sup>  $\text{p}K_{\text{a}}$  of triazole = 13.9<sup>51,54</sup>) could be mainly responsible for their capricious catalytic performances. In a previous report,<sup>56</sup> the azolate ionic liquids with the same anion, [bzim], displayed the highest CO<sub>2</sub> uptake ability due to its high nucleophilicities, which is in accord with its basicity. [P<sub>4444</sub>][bzim] and [P<sub>66614</sub>][bzim], with the same [bzim] anion, the catalytic activity was decreased with increasing

the hydrocarbon chain length of cations (Table 2, entries 3, 4). The same trend was observed in [P<sub>4444</sub>][triz] and [P<sub>66614</sub>][triz] (Table 2, entries 6, 7), which may be ascribed to the strong interactions between their anions and cations inducing changes in nucleophilicities of anions. The nucleophilicities are seen to be in accord with their basicities. The role of ionic liquid, in here is to activate CO<sub>2</sub> through nucleophilic addition to the anion whilst the organic cation may help solubilization of substrates.

In all cases, the selectivity was > 99.0 %, no by-products were found in <sup>1</sup>H NMR spectroscopy, within its detectable limits, except propylene carbonate, with conversion to propylene carbonate varying between 14.0 and 98.0 %. The best conversion rates were obtained with the most basic anion, benzimidazolite, and at highest temperatures (see Figure 2A). Notably, the yield of propylene carbonate increased dramatically with increasing temperatures. The increase of reaction temperature from 60.0 to 90.0 °C, not only shorten the reaction time but also improve the conversion to cyclic carbonate greatly (Table 2, entries 11-15). On increasing the reaction temperature to 100.0 °C, 93 % conversion was achieved within 2h (entry 16).



**Figure 2.** Effect of (A) reaction temperature and (B) CO<sub>2</sub> pressure on the yield of propylene carbonate using [P<sub>4444</sub>][bzim] ionic liquid. The red lines correspond to selectivity. Reaction conditions are given in Table 2. The errors associated with measuring (i) temperature was  $\pm 0.1$  °C; (ii) pressure was  $\pm 0.02$  MPa; (iii) NMR spectrometric integrals were  $\pm 2$  %

Although higher pressures favored good conversions (see Figure 2B), the yield was not overly sensitive to the CO<sub>2</sub> pressure. The propylene carbonate conversion increased smoothly as the CO<sub>2</sub> pressure increased from 0.25 to 0.75 MPa, while the CO<sub>2</sub> pressure had little effect on propylene carbonate conversion from 0.75 to 1.0 MPa. This indicates that there is a optimum CO<sub>2</sub> pressure influencing the efficiency of the reaction.

**Table 2.** Conversion of propylene oxide and CO<sub>2</sub> into the corresponding propylene carbonate by azolate ionic liquids<sup>a</sup>.

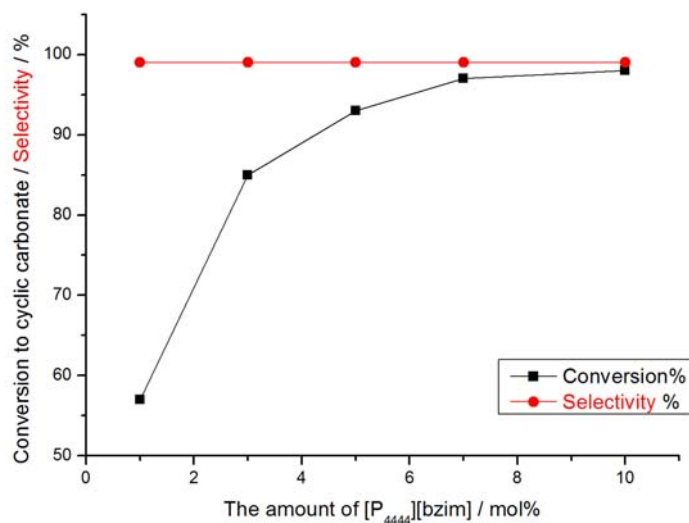
Entry	Ionic Liquid	Amount of IL/ mol%	<i>T</i> / °C	Time / h	Conversion to cyclic carbonate / % <sup>b</sup>
1	-	-	80.0	5.0	-
2	[P <sub>66614</sub> ][bzim]	5.0	25.0	24.0	trace
3	[P <sub>66614</sub> ][bzim]	5.0	80.0	5.0	74.0
4	[P <sub>4444</sub> ][bzim]	5.0	80.0	5.0	94.0
5	[N <sub>4444</sub> ][bzim]	5.0	80.0	5.0	80.0
6	[P <sub>66614</sub> ][triz]	5.0	80.0	5.0	70.0
7	[P <sub>4444</sub> ][triz]	5.0	80.0	5.0	75.0
8	[P <sub>4444</sub> ][bzim]	5.0	40.0	24.0	14.0
9	[P <sub>4444</sub> ][bzim]	5.0	50.0	24.0	54.0
10	[P <sub>4444</sub> ][bzim]	5.0	50.0	3.0	4.0
11	[P <sub>4444</sub> ][bzim]	5.0	60.0	24.0	62.0
12	[P <sub>4444</sub> ][bzim]	5.0	60.0	3.0	20.0
13	[P <sub>4444</sub> ][bzim]	5.0	70.0	3.0	41.0
14	[P <sub>4444</sub> ][bzim]	5.0	80.0	3.0	55.0
15	[P <sub>4444</sub> ][bzim]	5.0	90.0	3.0	81.0
16	[P <sub>4444</sub> ][bzim]	5.0	100.0	2.0	93.0
17	[P <sub>4444</sub> ][bzim]	5.0	120.0	2.0	96.0
18	[P <sub>4444</sub> ][bzim]	1.0	100.0	3.0	57.0

19	[P <sub>4444</sub> ][bzim]	3.0	100.0	2.0	85.0
20	[P <sub>4444</sub> ][bzim]	7.0	100.0	2.0	97.0
21	[P <sub>4444</sub> ][bzim]	10.0	100.0	2.0	98.0

<sup>a</sup> Reaction conditions: Propylene epoxide: 5.0 mmol, IL mol %: with respect to epoxide, stainless-steel autoclave (16.0 cm<sup>3</sup>), initial CO<sub>2</sub> pressure: 1.0 MPa; <sup>b</sup> Conversion to cyclic carbonate was determined by <sup>1</sup>H NMR spectroscopy. The errors associated with measuring (i) temperature was ± 0.1 °C; (ii) pressure was ± 0.02 MPa; (iii) NMR spectrometric integrals were ± 2 %

Since these reactions were best performed at elevated temperatures (80.0-100.0 °C), the thermal stability of azolate ionic liquids was assessed by TGA. The decomposition temperatures of the two triazolate ionic liquids ([P<sub>66614</sub>][triz], 245.0 °C; [P<sub>4444</sub>][triz], 241.0 °C) were below those of their benzimidazolate analogues ([P<sub>66614</sub>][bzim], 289.0 °C<sup>56</sup>; [P<sub>4444</sub>][bzim], 317.0 °C<sup>57,58</sup>). However, the tetrabutylammonium salt, [N<sub>4444</sub>][bzim], decomposed around 170.0 °C lower than its phosphonium analogue, indicative of the well-known base-initiated Hoffmann elimination.<sup>59-61</sup> Thus, for reactions at elevated temperatures, tetraalkylammonium salts should be avoided.

Finally, the effect of the mole ratio of epoxide: ionic liquid was studied. Demonstrably, the ionic liquid performs the role of a basic catalyst, as the epoxide is in significant excess. The almost quantitative conversion of propylene epoxide with a [P<sub>4444</sub>][bzim] loading of 7.0% (Table 2, entry 20) decreased to 57% when the concentration of [P<sub>4444</sub>][bzim] was 1.0% (Table 2, entry 18). The conversion to propylene carbonate did not increase with further increase in the catalyst loading from 7.0% to 10.0% (entries 20, 21). This indicates requirement of an optimum catalyst loading for efficient reaction. From data in Table 2 and Figure 3, it can clearly be seen that increasing the amount of ionic liquid increases the yield of product when other variables are kept constant. The yield of the cyclic carbonate levels out at 7.0-10.0 mol %, and even at 5.0 mol% the yield is only marginally reduced.



**Figure 3.** Effect of the amount of [P<sub>4444</sub>][bzim] on the conversion to propylene carbonate.


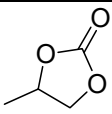
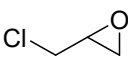
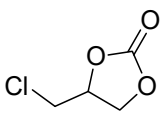
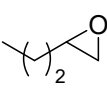
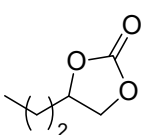
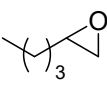
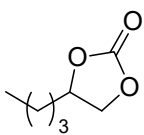
Moreover, not only minimising the quantity of catalyst is important, but also the catalyst needs to be recyclable. Recycling experiments were carried out under the optimum reaction conditions (100.0 °C, 2.0 h, 1.0 MPa). After vacuum removal of propylene carbonate, the recovered ionic liquid, [P<sub>4444</sub>][bzim], was reused for a further cycle under the same reaction conditions. After four cycles, only a slight lowering of conversion to cyclic carbonate (*ca.* 10.0 %) was observed (See ESI).

The optimal conditions were found to be 100.0 °C, 1.0 MPa CO<sub>2</sub> pressure, 2.0 h and with [P<sub>4444</sub>][bzim] (5.0 mol %), and these conditions were later used to study the reactions of a range of other epoxides (see Table 3).

**Reaction of other epoxides with CO<sub>2</sub>** Under the optimal reaction conditions (100.0 °C,  $P_{\text{CO}_2}$  = 1.0 MPa, 5.0 mol % [P<sub>4444</sub>][bzim], solvent-free), a range of different epoxides were investigated (Table 3). Remarkably, given the diversity of the precursors, conversion greater than 70.0 % were observed in all cases, with most of the products obtained in greater than 90.0 %.

Even though the yields of cyclic carbonates obtained using other methodologies (see Table 1; alternative reaction conditions and catalysts)<sup>36-46</sup> are comparable to the yields obtained in this work, the catalyst system that is employed here is devoid of metal salts or halides. The novel route reported here is significantly greener and more sustainable than any of the literature alternatives. In particular, the system can be recycled and offers facile product separation. It was noteworthy that, even with a sterically hindered, disubstituted symmetrical substrate such as cyclohexene oxide (Table 3, entry 7), the reaction could still proceed well, giving a reasonable conversion to the corresponding cyclic carbonate. Furthermore, epichlorohydrin (Table 3, entry 2) which carries an additional electrophilic centre also furnished a single product, *viz* cyclic carbonate, emphasising the superior selectivity.

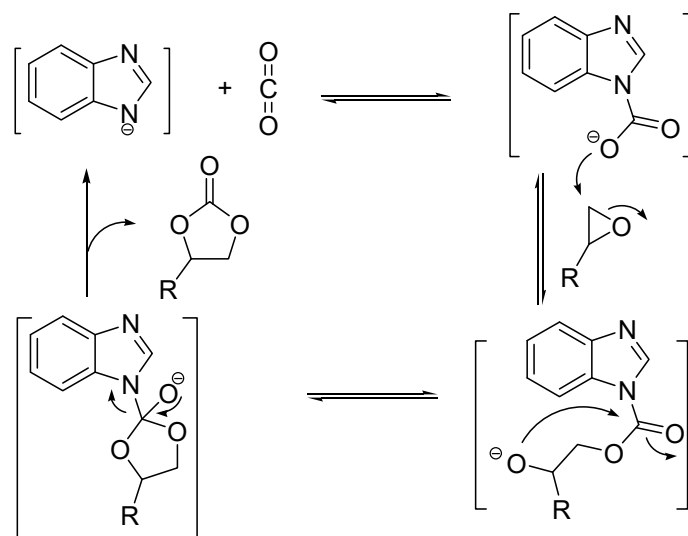
**Table 3.** Formation of cyclic carbonates from diverse epoxides and CO<sub>2</sub> in the presence of ionic liquid [P<sub>4444</sub>][bzim]<sup>a</sup>

Entry	Substrate	Product	Time / h	Conversion to cyclic carbonate / % <sup>b</sup>	Ref
1			2.0	90.3 <sup>c</sup>	19
2			3.0	88.4	19
3			3.0	90.2	18
4			3.0	95.4	62

5			3.0	89.1	63
6			4.0	88.3	19
7			3.0	71.2	18
8			3.5	90.4	19

<sup>a</sup> Reaction conditions: Epoxide (5.0 mmol), [P<sub>4444</sub>][bzim] (0.25 mmol, 93.8 mg), CO<sub>2</sub> (1.0 MPa) at 100.0 °C. <sup>b</sup> Isolated yield. <sup>c</sup> Conversion to cyclic carbonate was determined by <sup>1</sup>H-NMR spectroscopy. The errors associated with measuring (i) temperature was ± 0.1 °C; (ii) pressure was ± 0.02 MPa; (iii) NMR spectrometric integrals were ± 2 %

**Postulated reaction mechanism.** Based on the above data, a plausible mechanism for the reaction of epoxides with carbon dioxide, in the presence of basic ionic liquids, is proposed in Scheme 2. The first step in the mechanism would involve activation of carbon dioxide *via* nucleophilic attack of the azolate anion, producing an anionic carbamate intermediate. The oxygen of the carbamate group is electron rich, and undergoes a nucleophilic attack on the epoxide, causing it to ring-open. This is followed by an intramolecular cyclisation to produce a cyclic carbonate, whilst regenerating the original azolate anion. Alternatively, the azolate anion might attack the epoxide producing an oxo-nucleophile which then further reacts with carbon dioxide to yield the same final product. However, as there is no significant reaction observed between the azolate anion and the epoxide in the absence of CO<sub>2</sub>, this alternative mechanism would appear to be less likely.



**Scheme 2.** A plausible mechanism for cyclic carbonate formation catalysed by [P<sub>4444</sub>][bzim]. For simplicity, the spectator cation [P<sub>4444</sub>]<sup>+</sup> is omitted.

## CONCLUSION

In conclusion, several azolate ionic liquids were synthesised and tested as promoters in the cycloaddition reaction of CO<sub>2</sub> and epoxides. Using this protocol, a wide range of epoxide substrates, bearing alkyl, phenyl and halide groups, could be converted to the corresponding cyclic carbonates in good to excellent yields. The catalytic activity of the azolate ionic liquids is influenced significantly by the basicities of the anion, whereas the cation has largely a spectator role. Moreover, the ionic liquid could be recycled for several runs with little loss of activity. This suggests that treating epoxides with carbon dioxide in the presence of, in particular, tetrabutylphosphonium benzimidazolate, represents a new generic approach to the synthesis of cyclic carbonates. Moreover, the procedure not only utilises CO<sub>2</sub>, but is also highly efficient, green, halide- and metal- free, recyclable, and catalytic.



## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

The synthesis of [N<sub>4444</sub>][bzim] and the characterisation of azolate ionic liquids, <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS, TGA, DSC are listed.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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For Table of Contents Use Only

# Sustainable cyclic carbonate production, utilising carbon dioxide and azolate ionic liquids

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The azolate ionic liquids exhibit superior recyclability and provide non-halide catalyst system for CO<sub>2</sub> conversion.

