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Oxazolidinones Synthesis

Selective Synthesis of 5-Substituted *N*-Aryloxazolidinones by Cycloaddition Reaction of Epoxides with Arylcarbamates Catalyzed by the Ionic Liquid BmimOAc

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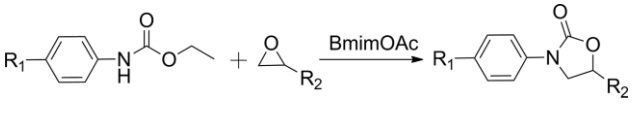
Abstract: A selective procedure for the synthesis of 5-substituted *N*-aryloxazolidinones by the coupling of epoxides with arylcarbamates catalyzed by ionic liquids has been developed. The effects of reaction time, reactant molar ratio, amount of catalyst, and temperature were investigated. Under the optimal reaction conditions, BmimOAc exhibited efficient catalytic activity compared with other ionic liquids leading to the formation of 5-substituted *N*-aryloxazolidinones in excellent yields. In addition, chiral 5-substituted oxazolidinones were synthesized by this procedure in good-to-excellent yields with enantiomeric excesses in excess of 99.9 % starting from chiral terminal epoxides. A possible reaction mechanism is discussed in accord with the results obtained by ^{1}H NMR spectroscopy and DFT calculations, which indicate the cooperative activation by BmimOAc through the formation of hydrogen bonds with the substrates.

Introduction

Oxazolidinones are important heterocyclic compounds in the field of fine chemicals and synthetic organic chemistry, and in recent decades they have received significant attention due to their outstanding biological activity. They have been used as a new class of antibiotics, HIV-1 protease inhibitors, fungicides, antibacterials, antimicrobial agents, and key structural units in pharmaceuticals as well as agrochemicals.[1]

Therefore, many strategies have been developed for the synthesis of oxazolidinones, including the reactions of amino alcohols with phosgene or its derivatives,[2] carbon dioxide with β-amino alcohols[3] or aziridines,[4] oxidative carbonylation of β-amino alcohols with CO/O_2,[5] and the carbonylation of β-amino alcohols with dialkyl carbonate.[6] However, these approaches required relatively harsh reaction conditions (5.0 MPa of CO_2 pressure, 110–180 °C, and a prolonged reaction time of 9–20 h) and the catalysts are highly toxic or expensive. In addition, synthetic approaches through cycloaddition reactions between isocyanates and epoxides, which are usually catalyzed by quaternary ammonium salts, lithium halides,[7] chromium(III) and vanadium(V) salen complexes, bimetallic aluminium (salen) complexes, or rare-earth-metal complexes,[8] have also been reported. However, these approaches suffer from high reaction temperature, long reaction time, and the use of toxic isocyanates. As an alternative process for the synthesis of oxazolidinones, the cycloaddition reaction between epoxides and carbamates has attracted significant attention due to the use of nontoxic materials. Many catalyst systems have been employed for this reaction, including binary metal oxides, organotin complexes, Al(aminotriphenolate) complexes, Co(III) salen complexes, and other alkaline agents.[9] Very recently, Deng and co-workers reported that amine-functionalized ionic liquids efficiently catalyzed the cycloaddition of epoxides with carbamates.[10] Good-to-excellent yields of 2-oxazolidinones were achieved, however, this process is limited to aliphatic carbamates.

During our studies on the utilization of ionic liquids as catalysts we have reported approaches to the synthesis of oxazolidinones by the straightforward conversion of CO_2 using epoxides and aromatic amines in the presence of ionic liquids, synergetic 1,8-diazobicyclo[5.4.0]undec-1-ene (DBU), and DBU-derived ionic liquids as catalysts, the direct condensation of 2-(arylamino) alcohols with diethyl carbonate, and the reaction of cyclic carbonates with aromatic amines in the presence of a catalytic amount of an ionic liquid.[11] Herein we wish to report our recent success in the synthesis of oxazolidinones in high yields and high regioselectivities by the coupling of epoxides with arylcarbamates in the presence of a catalytic amount of the ionic liquid BmimOAc (Scheme 1).



Scheme 1. Reaction of arylcarbamates with epoxides catalyzed by BmimOAc.

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Results and Discussion

Optimization of the Reaction Parameters and Catalyst System

Imidazolium-based ionic liquids are commonly known to act as reaction media and catalysts.[12] In our previous work on the synthesis of 3-aryloxazolidin-2-ones,[11b,11d] various ionic liquids exhibited different catalytic activities depending on their structures. On this basis we investigated the reactions of arylcarbamates with epoxides in the presence of a series of ionic liquids.

To optimize the reaction parameters and catalyst system, the reaction of ethyl phenylcarbamate with propylene oxide was performed in the presence of different catalysts and at different reaction times and reaction temperatures as well as with different amounts of catalyst and substrate molar ratios, as shown in Table 1. Without any catalyst, no conversion was observed (entry 1), which indicates that the catalyst is very important to activate the reaction. Upon addition of a catalytic amount of tetrabutylammonium acetate (TBAA), a yield of only 12 % was obtained (entry 2). When BmimOAc was used, the conversion reached 100 % with an isolated yield of 98 % of 5-methyl-3-phenyloxazolidin-2-one as the sole product (entry 3). Meanwhile, by using 1-butyl-2,3-dimethylimidazolium acetate (BmmimOAc), which bears a methyl group at C-2 of the imidazolium ring, a yield of 33 % (entry 4) was obtained, which is significantly lower than that obtained with the corresponding Bmim-based ionic liquid (entry 3). This implies that the cation of the ionic liquid plays a significant role in activating the reaction, which has previously been well established by us and others.[11b,11d,13] 1-Butyl-3-methylimidazolium chloride (BmimCl) and 1-butyl-3-methylimidazolium bromide (BmimBr) also gave lower yields of 70 and 57 %, respectively (entries 5 and 6). These results show that the yield of the product is also affected by the anion of the ionic liquid, with stronger hydrogen bond basicity,[14] which decreases in the order $OAc^- > Cl^- > Br^-$, giving higher yields.

Table 1. Optimization of the reaction conditions and catalyst system.[a]

Entry	Catalyst	Time [h]	*T* [°C]	EPC/PO molar ratio	Conv.[b] [%]	Yield[c] [%]
1	none	3	100	1:2	0	0
2	TBAA	3	100	1:2	15	12
3	BmimOAc	3	100	1:2	100	98
4	BmmimOAc	3	100	1:2	35	33
5	BmimCl	3	100	1:2	70	70
6	BmimBr	3	100	1:2	60	57
7	BmimOAc	2	100	1:2	80	77
8	BmimOAc	1	100	1:2	55	53
9	BmimOAc	3	90	1:2	85	84
10	BmimOAc	3	80	1:2	77	75
11	BmimOAc	3	100	1:1	40	40
12	BmimOAc	3	100	1:1.5	100	98
13	BmimOAc[d]	3	100	1:2	85	82
14	BmimOAc[e]	3	100	1:2	50	47

[a] Reagents and conditions: Ethyl phenylcarbamate (EPC; 5 mmol), propylene oxide (PO), EPC/PO molar ratio 1:1–1:3, 10 mol-% catalyst (based on EPC), 80–100 °C, 1–3 h. [b] Conversion of ethyl phenylcarbamate, determined by GC. [c] Isolated yield. [d] Reaction carried out with 5 % catalyst. [e] Reaction carried out with 1 % catalyst.

Next, using BmimOAc as catalyst, the reaction time was reduced to 2 and 1 h; the yield of the product fell to 77 and 53 %, respectively (entries 7 and 8). On lowering the reaction temperature from 100 to 90 and 80 °C, the yield decreased to 84 and 75 %, respectively (entries 9 and 10). Reducing the molar ratio from 1:2 to 1:1 led to a lower yield of the product (40 %; entry 11), whereas a ratio of 1:1.5 gave a similar yield of the product (entry 12). When the catalyst amount was decreased from 10 to 5 and 1 %, the yield dramatically dropped to 80 and 47 %, respectively (entries 13 and 14). Thus, the optimal reaction conditions for the coupling reaction between arylcarbamates and epoxides were found to be a molar ratio of 1:2, 10 % of catalyst, a reaction temperature of 100 °C, and a reaction time of 3 h.

Synthesis of 5-Substituted 3-Aryloxazolidin-2-ones from the Reaction of Arylcarbamates with Epoxides in the Presence of BmimOAc

The scope of the reaction was explored by studying the reactions of several arylcarbamates with various epoxides. The results are shown in Table 2.

Ethyl phenylcarbamate was easily converted into the corresponding oxazolidinones upon treatment with epoxides in the presence of a catalytic amount of BmimOAc. Ethylene oxide gave a high yield of 99 % of 3-phenyl-2-oxazolidinone (**1a**; Table 2, entry 1). Terminal epoxides bearing methyl, phenyl, and *n*-butyl groups gave excellent yields of 87–98 % of the corresponding 5-substituted oxazolidinones **1b**–**1d** (entries 2–4) as the sole products. Glycidyl phenyl ether gave a 95 % yield of **1e** (entry 5) and cyclohexene oxide gave a 53 % yield of **1f** (entry 6). The lower yield of **1f** might be attributed to the high steric hindrance of cyclohexene oxide. Ethyl (4-methoxyphenyl)carbamate and ethyl (4-ethoxyphenyl)carbamate, which have electron-donating groups, could also be used for this reaction and were smoothly converted into the corresponding 5-substituted 3-aryloxazolidin-2-ones **1g**–**1p** (entries 7–16) in yields ranging from 81 to 94 %. Ethyl (4-chlorophenyl)carbamate gave high yields of 85–94 % of **1q**–**1u** (entries 17–21), whereas ethyl (4-nitrophenyl)carbamate gave good yields of 68–80 % of **1v**–**1z** (entries 22–26); the lower yields were attributed to deactivation by the nitro group. In all cases the 5-substituted oxazolidinones were observed as the sole products and no byproducts were formed, which reveals that BmimOAc selectively catalyzes the ring-opening of epoxides to form the desired products.

Synthesis of Chiral 5-Substituted Oxazolidinones from the Reaction of Arylcarbamates with Chiral Epoxides in the Presence of BmimOAc

Chiral oxazolidinones have attracted significant attention in drug synthesis and have been used as synthetic and essential subunits in pharmaceuticals. To date, several synthetic approaches have been developed for the preparation of chiral 5-

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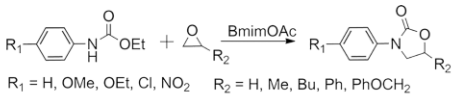
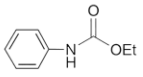
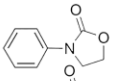
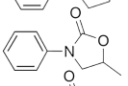
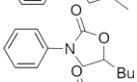
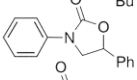
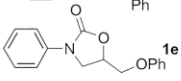
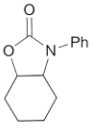
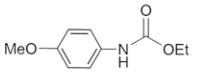
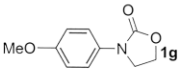
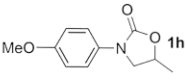
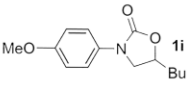
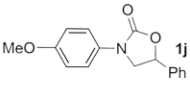
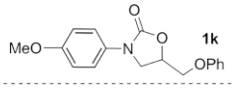
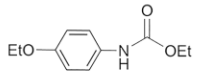
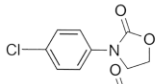
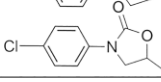
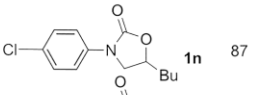
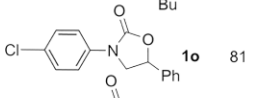
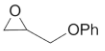
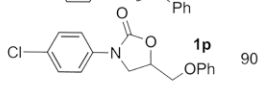
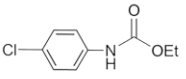
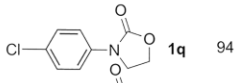
Table 2. Reaction of arylcarbamates with various epoxides.[a]



Entry	Aryl carbamte	Epoxide	Product	Yield[b] (%)
1			 **1a**	99
2			 **1b**	98
3			 **1c**	93
4			 **1d**	87
5			 **1e**	95
6			 **1f**	53[c]
7			 **1g**	94
8			 **1h**	93
9			 **1i**	92
10			 **1j**	85
11			 **1k**	90
12			 **1l**	93
13			 **1m**	90
14			 **1n**	87
15			 **1o**	81
16			 **1p**	90
17			 **1q**	94
18			**1r**	92
19			**1s**	89
20			**1t**	85
21			**1u**	93
22			**1v**	80
23			**1w**	73
24			**1x**	71
25			**1y**	68
26			**1z**	78

[a] Reagents and conditions: Arylcarbamates (5 mmol), epoxides (10 mmol), BmimOAc (0.5 mmol), 100 °C, 3 h. [b] Isolated yield. [c] Reaction was carried out at 120 °C for 6 h.

substituted oxazolidinones.[15] Herein we wish to report the synthetic application of the ionic liquid BmimOAc for the production of chiral oxazolidinones by the reaction of arylcarbamates with chiral terminal epoxides (Table 3). Arylcarbamates bearing electron-donating or -withdrawing groups were examined and in all cases regioselective ring-opening of the epoxides occurred and chiral 5-substituted oxazolidinones were obtained as the sole products. (*R*)-Propylene oxide was easily converted into the corresponding (*R*)-5-methyl-3-oxazolidin-2-ones **2a–2e** in yields ranging from 56 to 95 % with *ee* > 99.9 % (entries 1–5). On the other hand, (*S*)-propylene oxide gave (*S*)-5-methyl-3-oxazolidin-2-ones **2f–2j** in yields of 73–95 % with *ee* > 99.9 % (entries 6–10).

Studies of the Reaction Mechanism

The interactions between the substrates and ionic liquids were studied by ^{1}H NMR spectroscopy and DFT calculations with propylene oxide and ethyl phenylcarbamate used as models. A ^{1}H NMR titration based on the addition of aliquots of propylene oxide and ethyl phenylcarbamate to BmimOAc was carried out. Figure 1 shows the shift of the resonance of the 2-H of imidazolium upon interaction with propylene oxide. When 1 equiv. of propylene oxide was added to BmimOAc, the 2-H of the imidazolium cation shifted upfield from 10.51 to 10.15 ppm. This might be a result of a change in the hydrogen-bond donor–acceptor pair. In BmimOAc, the 2-H of the imidazolium cat-

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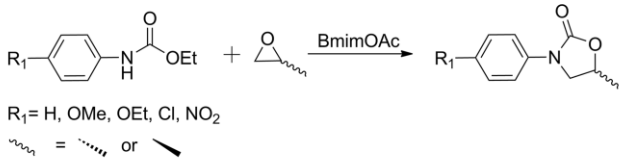
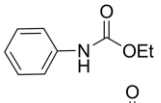
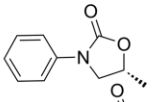
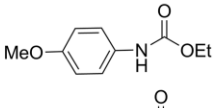
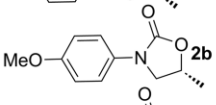
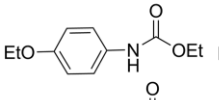
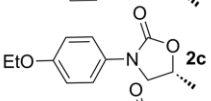
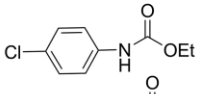
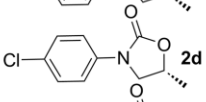
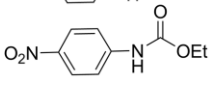
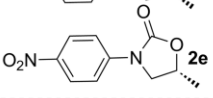
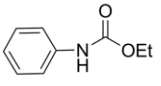
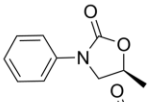
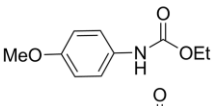
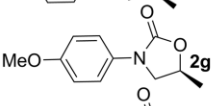
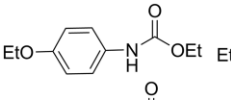
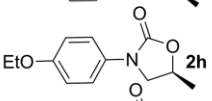
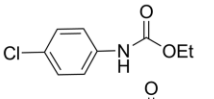
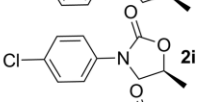
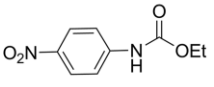
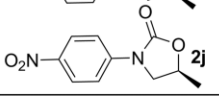
Table 3. Reaction of arylcarbamates with chiral terminal epoxides.[a]



Entry	Epoxide	Aryl carbamate	Product	Yield[b] %	ee[c] %
1			 **2a**	92	>99.9
2			 **2b**	95	>99.9
3			 **2c**	89	>99.9
4			 **2d**	92	>99.9
5			 **2e**	56	>99.9
6			 **2f**	95	>99.9
7			 **2g**	93	>99.9
8			 **2h**	82	>99.9
9			 **2i**	95	>99.9
10			 **2j**	73	>99.9

[a] Reagents and conditions: Arylcarbamates (5 mmol), epoxides (10 mmol), BmimOAc (0.75 mmol), 40 °C, 48 h. [b] Isolated yield. [c] Measured by HPLC.

ion acts as a hydrogen-bond donor to interact with the acetate counter ion, which, in turn, acts as a hydrogen-bond acceptor. After the stepwise addition of propylene oxide to BmimOAc, the intramolecular hydrogen bond between the acetate and 2-H is weakened and an intermolecular hydrogen bond between the imidazolium and propylene oxide emerges. These results imply that the propylene oxide could be activated by the 2-H of imidazolium.

It is clear that the 2-H of the imidazolium ring progressively shifts upon the addition of increasing amounts of propylene oxide due to its interaction with the oxygen atom of propylene oxide. Similar results have previously been reported by us and others.[11c,11d,16] Upon addition of 10 equiv. of propylene oxide, the 2-H resonance underwent a significant shift from δ = 10.51 to 9.60 ppm. This indicates that a stronger interaction between the 2-H of imidazolium and propylene oxide occurs when using an excess amount of propylene oxide. Meanwhile, when 10 equiv. of ethyl phenylcarbamate was added to the mixture of propylene oxide and BmimOAc, a dramatic shift in the reso-

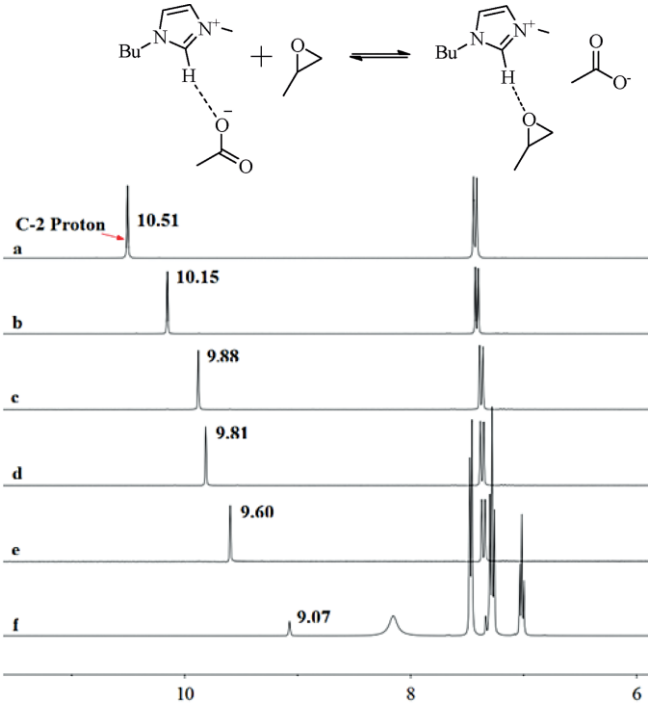


Figure 1. ^{1}H NMR spectra showing the shift of the 2-H resonance of BmimOAc in $CDCl_3$. a) BmimOAc, b) BmimOAc/propylene oxide = 1:1, c) 1:2, d) 1:5, e) 1:10 (mol ratio), respectively, f) BmimOAc/propylene oxide/ethyl phenylcarbamate = 1:10:10 (mol ratio).

nance of 2-H from δ = 9.60 to 9.07 ppm was observed. In a competitive environment, both the imidazolium and ethyl phenylcarbamate act as hydrogen-bond donors to interact with the acetate anion. Therefore, upon addition of ethyl phenylcarbamate, the acetate anion interacts with N–H, leaving the 2-H of the imidazolium cation free to interact with the oxygen atom of propylene oxide, resulting in the extreme upfield shift to δ = 9.07 ppm. This demonstrates that ethyl phenylcarbamate may be activated by the acetate anion through hydrogen bonding. These NMR studies have illustrated that BmimOAc could cooperatively activate ethyl phenylcarbamate and propylene oxide by hydrogen bonding.

To investigate the interaction between ethyl phenylcarbamate and BmimOAc alone, another ^{1}H NMR titration based on the addition of aliquots of the ionic liquid to ethyl phenylcarbamate was carried out and the results are shown in Figure 2.

When 1 equiv. of BmimOAc was added to ethyl phenylcarbamate, the peak of N–H underwent a downfield shift (from δ = 7.64 to 8.03 ppm). This demonstrates that ethyl phenylcarbamate could be activated by the interaction between N–H and the acetate counter ion of the ionic liquid. After the stepwise addition of further BmimOAc to ethyl phenylcarbamate, the N–H underwent a step-by-step downfield shift with peak broadening until it nearly disappeared after the addition of 10 equiv. of BmimOAc. This result can be explained by the acetate counter ion activating ethyl phenylcarbamate through hydrogen bonding.

The interactions between BmimOAc and the model substrates, propylene oxide and ethyl phenylcarbamate, were also

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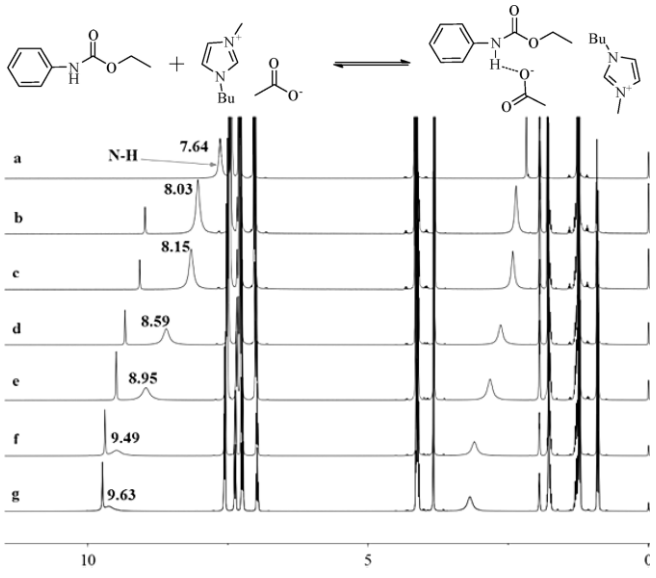


Figure 2. ^{1}H NMR spectra showing the shift of the N–H resonance of ethyl phenylcarbamate in $CDCl_3$. a) Ethyl phenylcarbamate, b) ethyl phenylcarbamate/BmimOAc = 1:1, c) 1:2, d) 1:3, e) 1:5, f) 1:7, g) 1:10 (mol ratio), respectively.

investigated by DFT calculations. The optimized geometrical structures of propylene oxide, ethyl phenylcarbamate, and the complex of propylene oxide and ethyl phenylcarbamate with BmimOAc were simulated at the B3LYP/6-31G level of theory (Figure 3). The length of the C^1–O^1 bond of propylene oxide is elongated from 1.492 to 1.511 Å after complexation with BmimOAc and the hydrogen bond O^1···H^2 is formed with a bond length of 1.966 Å. These results imply that propylene oxide is activated by a hydrogen-bonding interaction between the oxygen atom and the 2-H of the imidazolium ring of the ionic liquid. Meanwhile, the length of the N^1–H^1 bond of ethyl phenylcarbamate is elongated from 1.009 to 1.039 Å after complexation with BmimOAc and the hydrogen bond O^2···H^1 is formed with a bond length of 1.713 Å. This demonstrates that ethyl phenylcarbamate is activated by hydrogen bonding with the acetate anion. The results of these DFT calculations indicate that both the cation and anion of BmimOAc cooperatively activate the substrates through the formation of hydrogen bonds. This phenomenon has been well established by us in our previous work.[11c,11d]

Based on these results, a reaction mechanism is proposed in Scheme 2. First, the 2-H of the imidazolium cation activates the ring-opening of propylene oxide through the formation of a hydrogen bond with the oxygen atom. The activation of ring-opening of epoxides by this kind of interaction has also been reported previously.[17] At the same time, the acetate anion activates the ethyl phenylcarbamate through the formation of a hydrogen bond with the N–H atom. Secondly, the nitrogen atom of ethyl phenylcarbamate nucleophilically attacks the activated propylene oxide to form the intermediate species **iii**. Lastly, the species **iii** undergoes intramolecular cyclization to form the final product 5-methyl-3-phenyloxazolidin-2-one and BmimOAc is recycled to complete the reaction circle. When (*R*)-propylene oxide was used as reagent, (*R*)-5-methyl-3-phenyloxazolidin-2-ones was obtained as the final product with retention of configuration. A similar result was obtained with (*S*)-propylene oxide. These results indicate that the nitrogen atom of ethyl phenylcarbamate regioselectively attacks the propylene oxide at the carbon atom that has no chiral center to give intermediate **iii**, which in turn regioselectively undergoes ring closure to give the final product with retention of configuration.

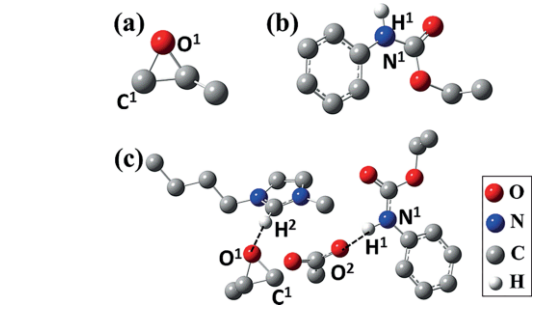
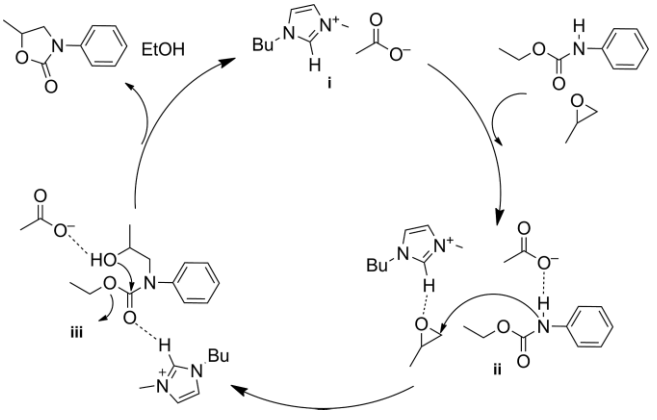


Figure 3. DFT-optimized geometries of a) propylene oxide, b) ethyl phenylcarbamate, and c) the complex of ethyl phenylcarbamate and propylene oxide with BmimOAc. Bond lengths: a) C^1–O^1 1.492 Å; b) N^1–H^1 1.009 Å; c) C^1–O^1 1.511 Å, N^1–H^1 1.039 Å, O^1···H^2 1. 966 Å, O^2···H^1 1.713 Å. Some hydrogen atoms have been omitted for clarity.



Scheme 2. Proposed mechanism for the reaction of ethyl phenylcarbamate with propylene oxide catalyzed by BmimOAc.

Conclusions

We have described a simple procedure for the synthesis of 5-substituted *N*-aryloxazolidinones by the coupling of epoxides with arylcarbamates catalyzed by ionic liquids. Under mild reaction conditions, BmimOAc can selectively catalyze the formation of various 5-substituted *N*-aryloxazolidinones in excellent yields. Moreover, this procedure is applicable to the synthesis of chiral 5-substituted oxazolidinones starting from chiral epoxides. The high catalytic activity of BmimOAc is attributed to the strong hydrogen-bond basicity of its anion and the hydrogen-bond acidity of the 2-H of its imidazolium ring. DFT calculations and ^{1}H NMR spectroscopy indicate that both the anion and cation of the ionic liquid cooperatively activate the substrates through the formation of hydrogen bonds.

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Experimental Section

General: Ethyl phenylcarbamate, propylene oxide, and other epoxides were supplied by TCI. (*S*/*R*)-Propylene oxides were purchased from Adamas-beta. All ionic liquids were supplied by Center of Green Chemistry and Catalysis, LICP, and CAS. The other reagents were commercial reagents of AR grade and were used without further purification. The arylcarbamates were synthesized by the reaction of arylamines with diethyl carbonate in the presence of the ionic liquid BmimOAc as catalyst (see the Supporting Information). GC analysis was performed by using a Shimadzu GC-14B instrument equipped with a DM-1701capillary column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector. The NMR spectra were recorded with Bruker Ascend 400 and DRX500 spectrometers with tetramethylsilane as the internal standard. HRMS analyses were performed with a Bruker Microtof II instrument. The enantiomeric excesses (*ees*) were determined by HPLC analysis, which was performed with an Agilent series instrument and a Daicel Chiralcel OD-H column. The DFT calculations were carried out by using the B3LYP functional with the 6-311g basis set as implemented in the Gaussian 09[18] program package. Vibrational frequency calculations, from which the zero-point energies were derived, were performed for each optimized structure at the same level of theory to identify the natures of all the stationary points.

General Procedure for Synthesis of 5-Substituted Oxazolidinones from the Reaction of Arylcarbamates with Epoxides: In a typical procedure, the reactions of arylcarbamates with epoxides were carried out in a 15 mL thick-walled pressure bottle. Arylcarbamates (5.0 mmol), epoxides (10.0 mmol), and BmimOAc (10 %, 0.5 mmol, 0.10 g) were mixed together and stirred at 100 °C for 3 h. The reaction mixtures were analyzed by GC with *n*-dodecane as the internal standard. The pure products were obtained by chromatography on silica gel and structurally characterized by NMR spectroscopy.

General Procedure for Synthesis of Chiral 5-Substituted Oxazolidinones from the Reaction of Arylcarbamates with Chiral Terminal Epoxides: In a typical procedure, the reactions of arylcarbamates with epoxides were carried out in a 15 mL thick-walled pressure bottle. Arylcarbamates (5.0 mmol), chiral epoxides (10.0 mmol), and BmimOAc (15 %, 0.75 mmol, 0.15 g) were mixed together and stirred at 40 °C for 48 h. The reaction mixtures were analyzed by GC with *n*-dodecane as the internal standard. The pure products were obtained by chromatography on silica gel and structurally characterized by NMR spectroscopy. The enantiomeric excesses (*ee* values) were determined by HPLC analysis.

Acknowledgments

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Keywords: Homogeneous catalysis · Reaction mechanisms · Cycloaddition · Ionic liquids · Nitrogen heterocycles

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