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Full Paper

Cyclic-Carbonate Synthesis

Synthesis of Functionalized Cyclic Carbonates by One-Pot Reactions of Carbon Dioxide, Epibromohydrin, and Phenols, Thiophenols, or Carboxylic Acids Catalyzed by Ionic Liquids

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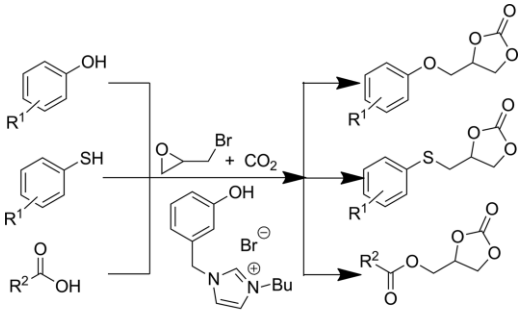
Abstract: The one-pot reactions of CO_2, epibromohydrin, and phenols, thiophenols, or carboxylic acids catalyzed by 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide were investigated. Three kinds of cyclic carbonates with ether, thioether, or ester groups were synthesized under mild reaction conditions in good-to-high yields. Reaction-mechanism studies indicated that the proton exchange between the alkoxide formed through the ring-opening reaction of epibromohydrin with 1-bromo-3-phenoxy-2-propanol plays a crucial role in this synthetic route. The catalyst 1-butyl-3-[(3-hydroxyphenyl)methyl]-imidazolium bromide was transformed to the corresponding cyclic-carbonate-functionalized ionic liquid during the reaction. This transformation did not affect its catalytic performance in the reaction.

Introduction

Cyclic carbonates are valuable organic compounds and have been used widely as polar aprotic solvents, electrolytes for lithium-ion batteries, and constituents of oils. Cyclic carbonates are also important intermediates and raw materials in the production of polycarbonates and polyurethanes.[1] In particular, cyclic carbonates with different functional groups are used as monomers to tailor the properties of polyesters.[2] Through the incorporation of different functional groups into the polymer backbone, polycarbonates usually show unique properties, such as hydrophilicity, biodegradation rates, and bioadhesion.

Carbon dioxide is a main greenhouse gas, which causes climate change, and also an abundant, nontoxic, nonflammable, readily available, and renewable carbon resource.[3] However, the transformation of CO_2 is a difficult task because CO_2 is the most oxidized state of carbon and is a thermodynamically stable molecule. The biggest obstacle to the establishment of a transformation processes is the low energy level of CO_2.[4] Therefore, the transformation of CO_2 generally requires a large energy input, such as harsh reaction conditions or the utilization of high-energy starting materials.

In the last decade, the cycloaddition of CO_2 with epoxides to produce five-membered cyclic carbonates has become one of the most successful routes for the utilization of CO_2.[5] This strategy employs the inherent high-energy of epoxides to overcome the thermodynamic stability of CO_2 molecules. Many catalytic systems including metal oxides,[6] alkali-metal salts,[7] transition-metal halides,[8] complexes,[9] Schiff bases,[10] functional polymers,[11] and ionic liquids[12] were developed to achieve the transformation of cyclic carbonate under mild reaction conditions. Recently, we have been interested in the reactions of CO_2, epoxides, and a third component catalyzed by ionic liquids.[13] In particular, we found that amino-functionalized cyclic carbonates could be synthesized through the one-pot reaction of CO_2, epihalohydrin, and aniline.[13a] Therefore, we envisioned that epihalohydrins would serve as ideal substrates for the development of a new efficient approach to synthesize various functionalized cyclic carbonates. Herein, 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide was first applied to catalyze the reactions of CO_2, epibromohydrin, and phenols, thiophenols, or carboxylic acids (Scheme 1). By this



Scheme 1. Synthesis of functionalized cyclic carbonates through the reactions of CO_2, epibromohydrin, and phenols, thiophenols, or carboxylic acids.

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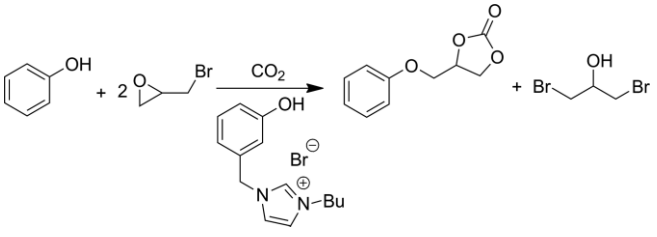
method, three kinds of functionalized cyclic carbonates with ether, thioether, and ester groups were successfully synthesized under mild reaction conditions.

Results and Discussion

Synthesis of Ether-Functionalized Cyclic Carbonates through One-Pot Reactions of CO_2, Epibromohydrin, and Phenols

The synthesis of 3-phenoxy-1,2-propylene carbonate by the cycloaddition of 2-(phenoxymethyl)oxirane with CO_2 has been reported widely.[14] 2-(Phenoxymethyl)oxirane is usually synthesized through the reaction of phenol and epihalohydrin in the presence of alkali (such as NaOH).[15] If the one-pot conversion of phenol, epibromohydrin, and CO_2 to 3-phenoxy-1,2-propylene carbonate could be achieved under alkali-free conditions, the synthesis of 3-phenoxy-1,2-propylene carbonate would be simplified. Owing to its high catalytic activity in the cycloaddition of CO_2 with epoxides,[16a] 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide was used to catalyze the model one-pot reaction of CO_2, epibromohydrin, and phenol to synthesize 3-phenoxy-1,2-propylene carbonate. A preliminary experiment was conducted to identify the products from the reaction mixture (Scheme 2), and 3-phenoxy-1,2-propylene carbonate and 1,3-dibromo-2-propanol were detected by GC after the reaction.



Scheme 2. The reaction of CO_2, epibromohydrin, and phenol catalyzed by 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide.

Effect of Various Reaction Conditions

To optimize the reaction conditions, the influence of reaction parameters including time, temperature, CO_2 pressure, and amount of catalyst were investigated, as shown in Figure 1. As the reaction time was prolonged from 4 to 6 h, the yield of 3-phenoxy-1,2-propylene carbonate increased rapidly. For reaction times longer than 6 h, the yield reached 74 % and did not increase anymore (Figure 1a). As the reaction temperature increased from 50 to 60 °C, the yield of 3-phenoxy-1,2-propylene carbonate increased gradually. However, for a further temperature increase from 60 to 80 °C, the yield of the product decreased rapidly. The appropriate reaction temperature was 60 °C (Figure 1b). For an increase of the CO_2 pressure from 0.5 to 2.0 MPa, the yield of 3-phenoxy-1,2-propylene carbonate increased initially and then decreased rapidly. The appropriate CO_2 pressure was 1.0 MPa (Figure 1c). The increase of the amount of catalyst was beneficial to the formation of 3-phenoxy-1,2-propylene carbonate. However, when the amount of catalyst was more than 5.0 mmol-%, the yield of 3-phenoxy-1,2-propylene carbonate decreased dramatically (Figure 1d). These results showed that the yields of product decreased at

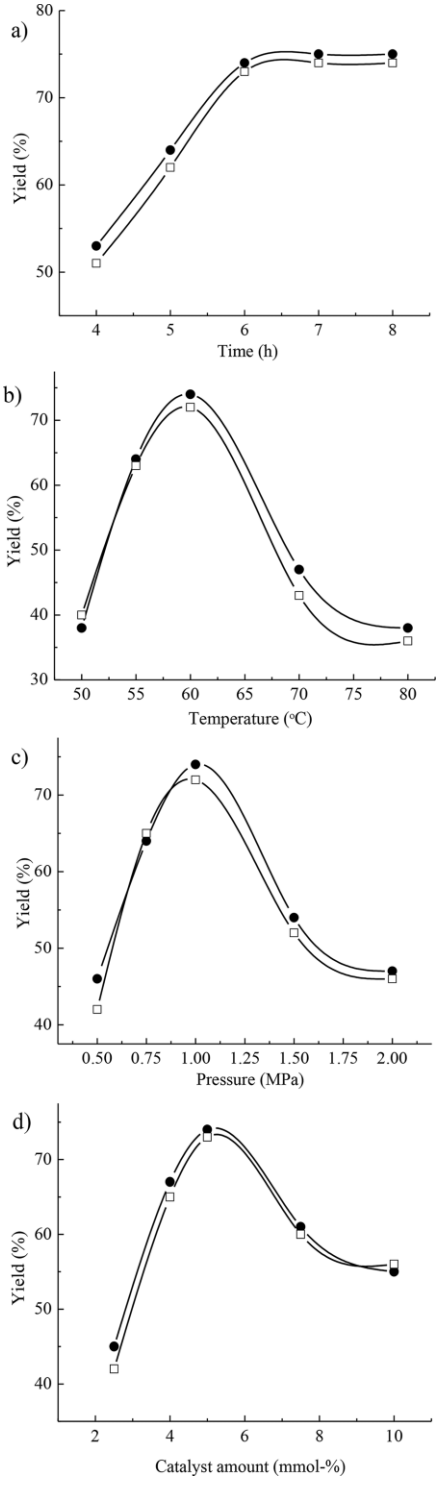


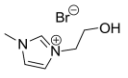
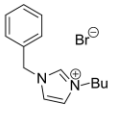
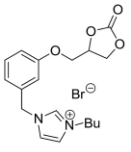
Figure 1. Effect of (a) reaction time, (b) reaction temperature, (c) CO_2 pressure, and (d) catalyst amount. Typical reaction conditions: phenol (1 mmol), epibromohydrin (5 mmol), CO_2 (1.0 MPa), ionic liquid (0.05 mmol), 60 °C, and 6 h. The yields of 3-phenoxy-1,2-propylene carbonate and 1,3-dibromo-2-propanol were calculated from the amount of phenol used. Circles: 3-phenoxy-1,2-propylene carbonate. Squares: 1,3-dibromo-2-propanol.

high temperature (>60 °C), high CO_2 pressure (>1.0 MPa), or high catalyst amount (>5.0 mmol-%). A possible reason is that the cycloaddition of CO_2 with epibromohydrin is accelerated under these conditions; therefore, the epibromohydrin is consumed and less is available to react with phenol. Under the abovementioned reaction conditions, the byproduct 1,3-dibromo-2-propanol formed in almost the same molar quantity as 3-phenoxy-1,2-propylene carbonate. In addition, when epichlorohydrin was used as the starting material under the optimized reaction conditions (60 °C, 1.0 MPa CO_2 pressure, and 5.0 mmol-% of catalyst), the yield of 3-phenoxy-1,2-propylene carbonate decreased to 40 %.

Reaction of CO_2, Epibromohydrin, and Phenol Catalyzed by Various Ionic Liquids

Various ionic liquids were applied to catalyze the reaction of CO_2, epibromohydrin, and phenol under the optimized reaction conditions (Table 1). When 1-(2-hydroxylethyl)-3-methylimidazolium bromide, 3-benzyl-1-butylimidazolium bromide, and 1-butyl-3-methylimidazolium bromide were used as the catalysts, the yield of 3-phenoxy-1,2-propylene carbonate reached 62, 48, and 53 % respectively (Table 1, Entries 1–3). These ionic liquids gave lower catalytic activities than that of 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide (74 % yield). These results implied that 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide was a highly efficient catalyst for the reaction of CO_2, epibromohydrin, and phenol. Furthermore, the cyclic-carbonate-functionalized ionic liquid, derived from the transformation of 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide during the reaction (see the Supporting Information, Scheme S1), exhibited similar catalytic performance to that of 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide, and the yield of 3-phenoxy-1,2-propylene carbonate reached 76 % (Table 1, Entry 4). Therefore, the transformation of 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide did not affect its catalytic performance in the reaction.

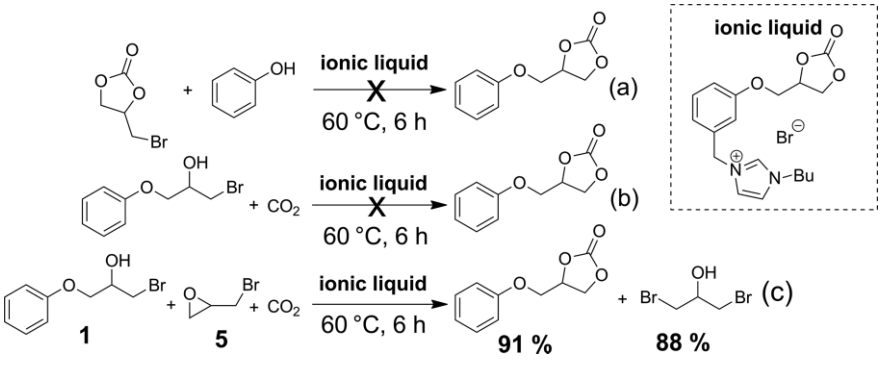
Table 1. The catalytic activities of various ionic liquids.[a]

Entry	Ionic liquid	Yield (%)[b]
1		62
2		48
3		53
4		76

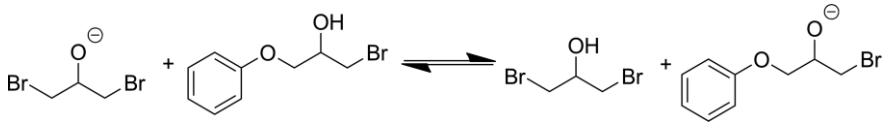
[a] Reaction conditions: phenol (1 mmol), epibromohydrin (5 mmol), CO_2 (1.0 MPa), ionic liquid (0.05 mmol), 60 °C, 6 h. [b] GC yield.

Reaction-Mechanism Studies

To investigate the reaction mechanism, three model reactions were performed, as shown in Scheme 3. 3-Bromo-1,2-propylene carbonate, which was obtained by the cycloaddition of CO_2 with epibromohydrin, did not react with phenol (Scheme 3a). 1-Bromo-3-phenoxy-2-propanol, which was formed by the reaction of phenol and epibromohydrin, did not react with CO_2 (Scheme 3b). However, when epibromohydrin was added to a mixture of 1-bromo-3-phenoxy-2-propanol and CO_2, 1-bromo-3-phenoxy-2-propanol was converted to 3-phenoxy-1,2-propylene carbonate, and 1,3-dibromo-2-propanol was obtained as a byproduct (Scheme 3c). The yields of 3-phenoxy-1,2-propylene carbonate and 1,3-dibromo-2-propanol reached 91 and 88 %, respectively. These results indicated that epibromohydrin plays an important role in the transformation of 1-bromo-3-phenoxy-2-propanol into 3-phenoxy-1,2-propylene carbonate. It has been reported that alkoxides form through the ring-opening reactions of epoxides through the nucleophilic attack of anions in ionic liquids.[16a] The generation of 1,3-dibromo-2-propanol indicated that proton exchange had occurred between 1-bromo-3-phenoxy-2-propanol and the alkoxide formed from the ring-opening reaction of epibromohydrin through the nucleophilic attack of a Br^- ion (Scheme 4). The deprotonated 1-bromo-3-phenoxy-2-propanol formed by proton exchange



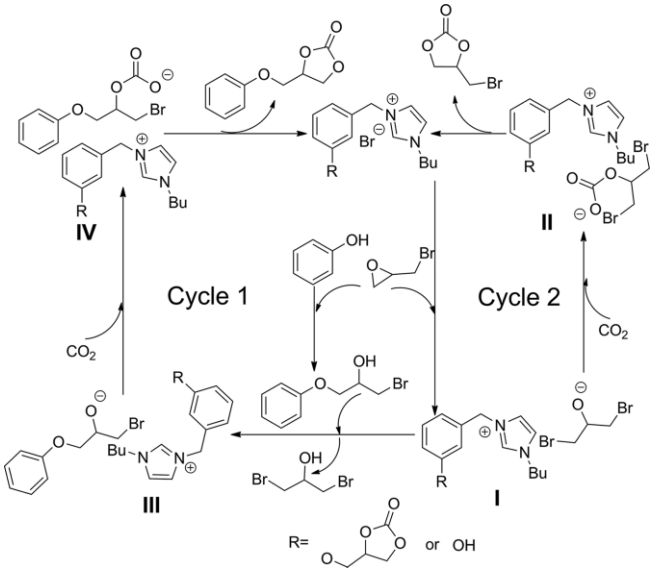
Scheme 3. Model reactions for the synthesis of 3-phenoxy-1,2-propylene carbonate.



Scheme 4. The possible proton exchange between the 1,3-dibromo-2-propanolate anion and 1-bromo-3-phenoxy-2-propanol.

would react with CO_2 to afford 3-phenoxy-1,2-propylene carbonate.

On the basis of the above analysis and previous reports,[16] a possible reaction mechanism including two catalytic cycles is proposed in Scheme 5. In cycle 1, epibromohydrin is initially transformed into intermediate **I** through the nucleophilic attack of the Br^- ion. At the same time, phenol reacts with epibromohydrin to afford 1-bromo-3-phenoxy-2-propanol in the presence of an ionic liquid. Then, equimolar amounts of 1,3-dibromo-2-propanol and intermediate **III** are generated by the proton exchange between intermediate **I** and 1-bromo-3-phenoxy-2-propanol. Thirdly, intermediate **III** reacts with CO_2 to afford intermediate **IV**. Lastly, the cyclization of intermediate **IV** through an intramolecular nucleophilic attack leads to the formation of 3-phenoxy-1,2-propylene carbonate and the regeneration of the catalyst. In cycle 2, intermediate **I** that did not take part in proton exchange reacts with CO_2 to afford **II**. Then, the cyclization of intermediate **II** through an intramolecular nucleophilic attack leads to the formation of 3-bromo-1,2-propylene carbonate and the regeneration of the catalyst.

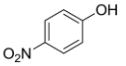
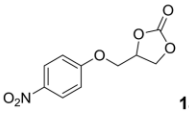
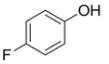
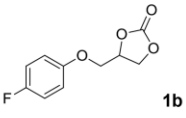
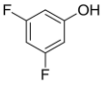
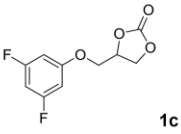
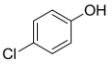
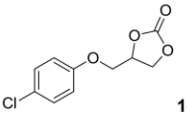
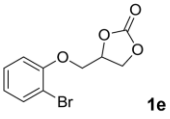
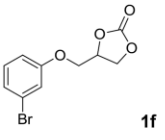
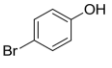
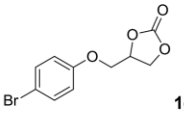
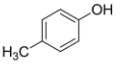
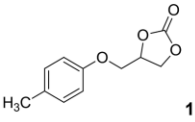
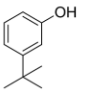
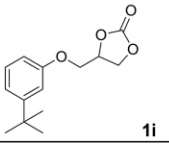


Scheme 5. Proposed reaction mechanism.

Synthesis of Ether-Functionalized Cyclic Carbonates from CO_2, Epibromohydrin, and Substituted Phenols

To investigate the generality of this procedure, the reactions of CO_2, epibromohydrin, and substituted phenols were investigated under the optimized reaction conditions (Table 2). Substituted phenols with strong electron-withdrawing groups (Table 2, Entries 1–3) could be transformed into the corresponding cyclic carbonates in high yields. When 4-nitrophenol, 4-fluorophenol, and 3,5-difluorophenol were used as substrates, the yields of **1a**, **1b** and **1c** reached 85, 79, and 70 % respectively. Phenols with weak electron-withdrawing groups including chlorophenol and bromophenol (Table 2, Entries 4–7) were also converted smoothly to the corresponding cyclic carbonates **1d**–**1g** in yields ranging from 51–66 %. However, when phenols with electron-donating groups, that is, 3-*tert*-butylphenol and

Table 2. Reactions of CO_2, epibromohydrin, and substituted phenols catalyzed by 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide.[a]

Entry	Substrate	Product	Yield (%)[b]
1		 **1a**	85
2		 **1b**	79
3		 **1c**	70
4		 **1d**	66
5		 **1e**	61
6		 **1f**	57
7		 **1g**	51
8		 **1h**	43
9		 **1i**	41

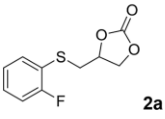
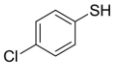
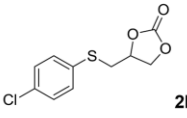
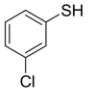
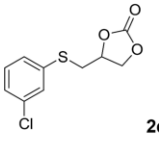
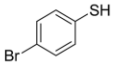
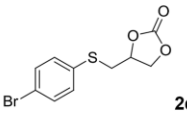
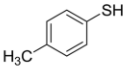
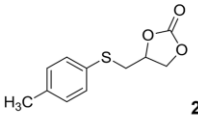
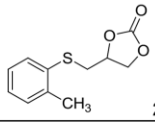
[a] Reaction conditions: substituted phenol (1 mmol), epibromohydrin (5 mmol), CO_2 (1.0 MPa), ionic liquid (0.05 mmol), 60 °C, 6 h. [b] Isolated yield.

4-methylphenol (Table 2, Entries 8 and 9), were used as substrates, the yields of the corresponding cyclic carbonates **1h** and **1i** were only 43 and 41 %, respectively. These results showed that the activities of phenols with electron-withdrawing groups were better than those of phenols with electron-donating groups. A possible reason is that electron-withdrawing groups enhance the acidity of the phenol to promote its reaction with epibromohydrin.

Synthesis of Thioether-Functionalized Cyclic Carbonates by One-Pot Reactions of CO_2, Epibromohydrin, and Thiophenols

Taking advantage of our protocol for the preparation of ether-functionalized cyclic carbonates, we explored the reactions of CO_2, epibromohydrin, and thiophenols catalyzed by 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide (Table 3). Substituted thiophenols with electron-withdrawing groups, that is, 2-fluorobenzenethiol, 4-chlorobenzenethiol, 3-chlorobenzenethiol, and 4-bromobenzenethiol (Table 3, Entries 1–4), were transformed smoothly to the corresponding cyclic carbonates **2a**–**2d** in 71, 75, 65, and 68 % yield, respectively. However, when substituted thiophenols with electron-donating groups, that is, 4-methylbenzenethiol and 2-methylbenzenethiol, were used as substrates (Table 3, Entries 5 and 6), the yields of **2e** and **2f** were only 58 and 50 %. These results showed that thiophenols with electron-withdrawing groups exhibited higher activities than those of thiophenols with electron-donating groups owing to their stronger acidities.

Table 3. Reactions of CO_2, epibromohydrin, and substituted thiophenols catalyzed by 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide.[a]

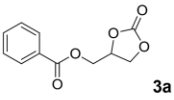
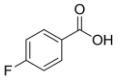
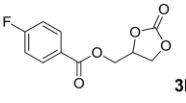
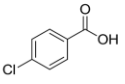
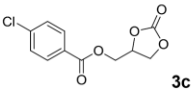
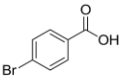
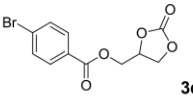
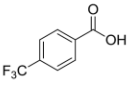
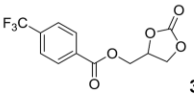
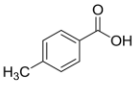
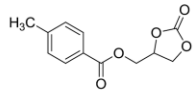
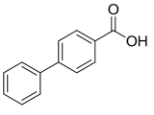
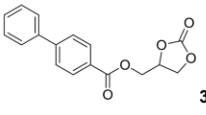
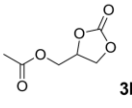
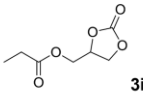
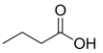
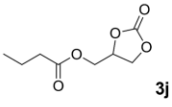
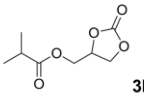
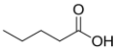
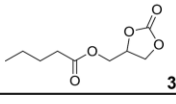
Entry	Substrate	Product	Yield (%)[b]
1		 **2a**	71
2		 **2b**	75
3		 **2c**	65
4		 **2d**	68
5		 **2e**	58
6		 **2f**	50

[a] Reaction conditions: substituted thiophenol (1 mmol), epibromohydrin (5 mmol), CO_2 (1.0 MPa), ionic liquid (0.05 mmol), 70 °C, 6 h. [b] Isolated yield.

Synthesis of Ester-Functionalized Cyclic Carbonates by One-Pot Reactions of CO_2, Epibromohydrin, and Carboxylic Acids

The first synthetic route to cyclic carbonates containing ester groups was reported by Ramaiah,[17] who synthesized 3-

Table 4. Reactions of CO_2, epibromohydrin, and carboxylic acids catalyzed by 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide.[a]

Entry	Substrate	Product	Yield (%)[b]
1		 **3a**	93
2		 **3b**	94
3		 **3c**	93
4		 **3d**	90
5		 **3e**	93
6		 **3f**	91
7		 **3g**	90
8		 **3h**	94
9		 **3i**	92
10		 **3j**	91
11		 **3k**	92
12		 **3l**	89

[a] Reaction conditions: carboxylic acid (1 mmol), epibromohydrin (5 mmol), CO_2 (1.0 MPa), ionic liquid (0.05 mmol), 60 °C, 6 h. [b] Isolated yield.

benzoyloxy-1,2-propylene carbonate through the reaction of glycerol carbonate and potassium benzoate. Subsequently, Dibenedetto et al.[18] reported the synthesis of cyclic carbonates with ester groups through the esterification of glycerol carbonate with different acyl chlorides under alkaline conditions. Recently, Climent et al.[19] developed a synthesis of ester-functionalized cyclic carbonates through the esterification of glycerol carbonate and carboxylic acid catalyzed by a Nafion–silica hybrid.

We next explored the new synthetic method for ester-functionalized cyclic carbonates through the reactions of CO_2, epibromohydrin, and carboxylic acids catalyzed by 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide (Table 4). When benzoic acids were used as the substrates, the yields of the corresponding cyclic carbonates **3a**–**3g** reached 90–94 % (Table 4, Entries 1–7).

Aliphatic carboxylic acids (Table 4, Entries 8–12) were also successfully converted into the corresponding cyclic carbonates **3h**–**3l** in 89–94 % yield. The high yields were attributed to the rapid generation of bromo alcohols through the reactions of the carboxylic acids with epibromohydrin catalyzed by the ionic liquid.[20] These results demonstrated that this procedure could achieve the transformation of carboxylic acids into ester-functionalized cyclic carbonates with high efficiency.

Conclusions

Three kinds of functionalized cyclic carbonates with ether, thioether, or ester groups were successfully synthesized through the one-pot reactions of CO_2, epibromohydrin, and phenols, thiophenols, or carboxylic acids catalyzed by 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide under mild reaction conditions. The catalyst 1-butyl-3-[(3-hydroxyphenyl)-methyl]imidazolium bromide was transformed into the corresponding cyclic-carbonate-functionalized ionic liquid during the reaction. This carbonate-functionalized ionic liquid showed similar catalytic activity to that of 1-butyl-3-[(3-hydroxyphenyl)methyl]imidazolium bromide. The study of the reaction mechanism indicated that proton exchange between an alkoxide and 1-bromo-3-phenoxy-2-propanol plays a crucial role in this synthetic route.

Experimental Section

General Information: CO_2 was supplied by Doumaoai with a purity of 99.995 %. All solvents were supplied by Sinopharm Chemical Reagent Company. Epibromohydrin, phenol, phenylthiol derivatives, and carboxylic acids were purchased from TCI. The NMR spectra were recorded with Bruker Ascend 400 instruments with tetramethylsilane (TMS) as an internal standard. GC analysis was performed with a Shimadzu GC-14B instrument equipped with a DM-1701 capillary column (60 m, 0.32 mm, 0.25 μm) and a flame-ionization detector. HRMS analyses were performed with a Bruker Microtof II instrument.

1-Butyl-3-[(3-hydroxyphenyl)methyl]imidazolium Bromide: 3-Bromomethylphenol (0.935 g, 5 mmol) and butylimidazole (4 mL) were heated at 120 °C for 12 h. The suspension was cooled to room temperature, washed with Et_2O (3×30 mL), and dried under vacuum at 70 °C to afford a light yellow viscous oil in 75 % yield. ^1H NMR (400 MHz, [D_6]DMSO, TMS): δ = 9.64 (s, 1 H), 9.48 (s, 1 H), 7.88 (d, J = 8.0 Hz, 2 H), 7.20 (t, J = 8.0 Hz, 1 H), 6.84–6.80 (m, 3 H), 5.39 (s, 2 H), 4.21 (t, J = 6.0 Hz, 2 H), 1.80–1.76 (m, 2 H), 1.28–1.22 (m, 2 H), 0.89 (t, J = 8.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO, TMS): δ = 157.78, 136.11, 130.00, 122.70, 122.61, 118.51, 115.61, 114.94, 51.84, 48.65, 31.25, 18.76, 13.23 ppm.

General Procedure for the Synthesis of 3-Phenoxy-1,2-propylene Carbonates through the One-Pot Conversion of CO_2, Epibromohydrin, and Phenol Catalyzed by 1-Butyl-3-[(3-hydroxyphenyl)methyl]imidazolium Bromide: In a typical experiment, phenol (0.094 g, 1 mmol), epibromohydrin (0.685 g, 5 mmol), and catalyst (0.016 g, 0.05 mmol) were added to a stainless-steel autoclave with an inner volume of 50 mL. The autoclave was heated at 60 °C for 2 h, the pressure of CO_2 was adjusted to 1.0 MPa, and heating was continued at 60 °C for 4 h. The autoclave was cooled naturally to room temperature, and the remaining CO_2 was removed slowly. The product was analyzed by GC, and the pure product was obtained by silica gel chromatography and characterized by NMR spectroscopy and HRMS.

The one-pot reactions of CO_2, epibromohydrin, and 4-chlorothiophenol or carboxylic acid were performed by similar procedures. The difference was that the autoclave was pressurized with 1.0 MPa of CO_2 at ambient temperature and then heated for 6 h at 70 or 60 °C, respectively.

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Keywords: Carbon dioxide · Oxygen heterocycles · Ionic liquids · Cyclic carbonates · Synthesis design

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