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Ionic Liquid as an Efficient Promoting Medium for Fixation of CO₂: Clean Synthesis of α-Methylene Cyclic Carbonates from CO₂ and Propargyl Alcohols Catalyzed by Metal Salts under Mild Conditions

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Reactions of propargyl alcohols with CO₂ in a [BMIm][PhSO₄]/CuCl catalytic system to produce the corresponding α-methylene cyclic carbonates were conducted with high yields. Mild reaction conditions, enhanced rates, improved yields, and recyclable ionic liquid catalyst systems are the remarkable features exhibited in this process. Furthermore, the use of large amounts of tertiary amines as well as nitrogen-containing organic solvents as employed in previously studies was avoided.

Introduction

Development of green processes based on chemical fixation of carbon dioxide (CO₂) has received a great deal of interest in recent years because carbon dioxide could be used as a safe and cheap C₁ building block to produce useful organic compounds. A large number of studies have been devoted to the fixation of CO₂ for synthesis of alkylidene carbonates, which are usually obtained from reactions between CO₂ and propargyl alcohols catalyzed over various metal complexes including Cu, Co, Ru, and Pd or in the presence of large amounts of tertiary phosphines, because the five-membered ring alkylidene carbonates are important intermediates for many organic syntheses. However, the use of tertiary amines, large amounts of organic solvents, and high CO₂ pressure (ca. 5.0 MPa) was unavoidable in order to achieve good results. Additionally, this reaction usually proceeded in volatile organic solvents, such as DMF or THF. Therefore, it is necessary to develop a mild, clean, and efficient method for the synthesis of alkylidene carbonates from carbon dioxide.

Room temperature ionic liquids, especially those based on the 1-alkyl-3-methylimidazolium cations, have shown great promise as an attractive alternative to conventional organic solvents, and much attention has been currently focused on organic reactions promoted by ionic liquids. They are nonvolatile, recyclable, nonexplosive, easily operable, and thermally robust. Recently, it was shown that these novel materials had good dissolvability for many gaseous substrates, such as CO₂, which suggests that they should be an effective medium for fixation of carbon dioxide. In our previous work, it was found that an ionic liquid could be an effective catalyst system for cycloaddition of CO₂ with propylene oxide and direct synthesis of symmetrical dialkylurea from CO₂ and aliphatic amines. With our continuous research in the fixation of CO₂ using ionic liquid catalyst system, here,

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we report an efficient and environmentally benign method for synthesis of α-methylene cyclic carbonates from CO2 and propargyl alcohols catalyzed by transition metal salts in ionic liquid without any other cocatalysts and organic solvents (Scheme 1).

**Results and Discussion**

The results of the preliminary screening of commercially available transition metal salts as catalysts for the reaction in ionic liquid 1-butyl-3-methylimidazolium benzene sulfonate ([BMI|m]PF6) are summarized in Table 1. It can be seen that high yield was achieved over catalyst CuCl, and similar results were also obtained over CuBr and CuI (entries 1–3). The only byproduct detected was 3-hydroxyl-3-methyl-2-butanone in a [BMI|m][PhSO3] system. This may be formed due to the hydrolysis of α-methylene cyclic carbonate with water in the ionic liquid. As for β-oxopropyl carbonate, which was formed by further reaction of α-methylene cyclic carbonate with 3-hydroxyl-3-methyl-2-butanone and had been isolated in a K2CO3/crown ether system, it was not detected here. The subsequent experiments of yield dependences with temperatures and CO2 pressure revealed that 1.0 MPa of initial CO2 pressure and 120 °C were necessary to achieve good results since the conversions only reached to 39% and 65%, respectively, with a lower reaction temperature or decreased CO2 pressure, such as 90 °C or 0.5 MPa (entries 4 and 5). The catalytic activities of several other metal salts such as CoCl2, CuCl2, ZnCl2, RuCl3 and RhCl3, etc., were also investigated, while poor results were obtained except 80% of yield was achieved when using CuCl2 as catalyst (entry 6 to 18). It was reported that the reaction of propargyl alcohol with dicyclopentadienyl cobalt as catalyst gave the carbonate with the maximum yield of 87% in a traditional organic solvent system. Such great differences in catalytic performances may be derived from different ligands of cobalt and reaction media, although the detailed mechanism is still not clear at this stage. It is worth noting that no desired α-methylene cyclic carbonate was produced, although the substrate could be effectively converted when noble metal salts, such as Pd(II), Rh(III), Ru(III), Au(III), were used as catalysts. Some black tar could be seen on the inner wall of the reactor after reaction, which suggested that polymerization may occur during the reaction with these noble metal salts ([BMI|m][PhSO3]) systems. In the absence of metal salt as catalyst, the reaction did not yield any product even after a long reaction time (entry 19).

Using CuCl as catalyst, the reaction between CO2 and 2-methyl-3-butyn-2-ol was also investigated in some other ionic liquids and organic solvents, and the corresponding results were listed in Table 2. In comparison with the results obtained from organic solvents, the catalytic efficiency and yields could be greatly enhanced in ionic liquids and organic solvents, and the corresponding results were listed in Table 2. In comparison with the results obtained from organic solvents, the catalytic efficiency and yields could be greatly enhanced in ionic liquids and organic solvents, and the corresponding results were listed in Table 2. In comparison with the results obtained from organic solvents, the catalytic efficiency and yields could be greatly enhanced in ionic liquids and organic solvents, and the corresponding results were listed in Table 2. In comparison with the results obtained from organic solvents, the catalytic efficiency and yields could be greatly enhanced in ionic liquids and organic solvents, and the corresponding results were listed in Table 2. In comparison with the results obtained from organic solvents, the catalytic efficiency and yields could be greatly enhanced in ionic liquids and organic solvents, and the corresponding results were listed in Table 2. In comparison with the results obtained from organic solvents, the catalytic efficiency and yields could be greatly enhanced in ionic liquids and organic solvents, and the corresponding results were listed in Table 2.
was known to be an acidic ionic liquid. If the imidazolium cation was substituted by a pyridinium cation, 78% of yield was obtained (entry 6), indicating that both cation and anion played important roles as the reaction media, although the mechanism was not clear. Other organic solvents, including dichloromethane, toluene, tetrahydrofuran, dioxane, dimethyl sulfoxide (DMSO), and tetramethylene sulfone, were also employed as reaction media, and the conversions of 2-methyl-3-butyn-2-ol were all less than 10% (entries 8 to 12). Furthermore, in the nitrogen-containing molecular solvents, such as nitromethane and $N,N$-dimethylacetamide (DMAc), the reaction rate could be improved to a certain extent but the maximum yield was only about 40% (entries 14 and 15). No R-methylene cyclic carbonate could be detected when the reaction was performed under solvent-free conditions, indicating that the nitrogen-containing solvents should be the key factor to promote this process (entry 16).

Using a $[\text{BMIm}]\,[\text{PhSO}_3]$--CuCl catalytic system, the reactions of CO$_2$ to several other R-ethynyl alcohols were also carried out, and the results were summarized in Table 3. The reaction of CO$_2$ to 3-methyl-1-pentyn-3-ol afforded the corresponding cyclic carbonate with a yield of 97% (entry 1). As it could be expected, higher conversion (97%) was also obtained with 3,5-dimethyl-1-hexyn-3-ol as substrate (entry 2). Treatment of 2-phenyl-3-butyln-2-ol with CO$_2$ in $[\text{BMIm}]\,[\text{PhSO}_3]$--CuCl system afforded the corresponding α-methylene cyclic carbonate derivative d with 45% of conversion (entry 3). In the case of secondary and primary propargylic alcohols as substrates, no desired products were detected, suggesting that such reactions seemed to be specific for tertiary alcohols (entries 4 and 5).

A tremendous advantage by using ionic liquids as a novel reaction medium as well as promoter for this transformation is that they could be easily recovered and reused after the end of the reaction. Direct distillation of the cyclic carbonates from the reaction mixture appears to be attractive in the case that the products are volatile enough. The copper catalysts immobilized in ionic liquids could be reused 3 times without losing activity (entry 6).

### Experimental Section

**General Methods.** $^1$H NMR (400 MHz) spectra were obtained as solutions in either CD$_2$COCOD$_2$ or D$_2$O. Chemical shifts were reported in parts per million (ppm, $\delta$) and referenced to TMS or D$_2$O ($\delta$ 4.88). Infrared spectra were recorded as a thin film on sodium chloride, and absorptions were reported in wavenumbers (cm$^{-1}$). Melting points are uncorrected. Distillations were performed using a Kugelrohr ball–tube distillation apparatus. Anhydrous organic solvents

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**TABLE 3. Reactions of CO$_2$ with Various Propargylic Alcohols Catalyzed by CuCl in $[\text{BMIm}]\,[\text{PhSO}_3]$**

<table>
<thead>
<tr>
<th>Entry</th>
<th>propargylic alcohols</th>
<th>Products</th>
<th>Conversion of alcohols (%)</th>
<th>Selectivity of cyclic carbonate yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\begin{align*} &amp; \text{HO} \ &amp; \text{HO} \end{align*}$</td>
<td>$\begin{align*} &amp; \text{O} \ &amp; \text{O} \end{align*}$</td>
<td>99</td>
<td>299</td>
</tr>
<tr>
<td>2</td>
<td>$\begin{align*} &amp; \text{HO} \ &amp; \text{HO} \end{align*}$</td>
<td>$\begin{align*} &amp; \text{O} \ &amp; \text{O} \end{align*}$</td>
<td>97</td>
<td>299</td>
</tr>
<tr>
<td>3</td>
<td>$\begin{align*} &amp; \text{HO} \ &amp; \text{O} \end{align*}$</td>
<td>$\begin{align*} &amp; \text{O} \ &amp; \text{O} \end{align*}$</td>
<td>45</td>
<td>299</td>
</tr>
<tr>
<td>4</td>
<td>$\begin{align*} &amp; \text{HO} \ &amp; \text{O} \end{align*}$</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>5</td>
<td>$\begin{align*} &amp; \text{HO} \ &amp; \text{O} \end{align*}$</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>6</td>
<td>$\begin{align*} &amp; \text{HO} \ &amp; \text{O} \end{align*}$</td>
<td>----</td>
<td>98</td>
<td>299</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: $[\text{BMIm}]\,[\text{PhSO}_3]$, 10 mmol; 2-methyl-3-butyn-2-ol, 1.68 g (20 mmol); CuCl, 0.04 g (0.4 mmol); CO$_2$, 10 atm; temperature, 120 °C; reaction time, 8 h.
were dried and then distilled prior to use. 2-Methyl-3-butyn-2-ol, 3-methyl-1-pentyn-3-ol, 3,5-dimethyl-1-hexyn-3-ol, and 2-phenyl-3-butyn-2-ol were not purified prior to use. All other chemicals used for synthetic procedures were reagent grade or better. Solutions were concentrated in vacuo with a rotary evaporator, and the residue was purified using a silica gel column unless specified otherwise.

**Synthesis of α-Methylene Cyclic Carbonates and Analyses.** All reactions were conducted in a 90 mL autoclave with a glass tube inside equipped with magnetic stirring. In each reaction, 10 mmol of ionic liquid, 20 mmol of propargylic alcohol, 0.4 mmol of catalyst, and 0.5–1.0 MPa of CO₂ were successively introduced and reacted at 90–120 °C for the desired period. After the reaction, the autoclave was cooled to room temperature, and then the reaction mixture was analyzed by GC. The isolation yield of desired product was obtained by direct vacuum distillation. Qualitative and quantitative analyses of organic products were conducted with HP 6890/5973 GC/MS and an HP 1790 GC equipped with FID detector. The concentrations of reactant and product were directly given by the system of GC chemstation according to the area of each chromatograph peak.

**Spectroscopic Data for Selective Products.**

**4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one (a):** white solid (2.48 g, 97%) distilled under reduced pressure (12 mmHg, bp 70–71 °C), mp 26–30 °C; δ_H (400 MHz, CD₃COCD₃) 4.75 (1H, d, J = 3.6 Hz), 4.56 (1H, d, J = 4.0 Hz), 1.65 (6H, s); ν/cm⁻¹ 1826 (C=O) and 1686 (C=C). GC–MS m/z = 128 (M⁺), 105, 84, 69, 56, 41. Anal. Calcd for C₆H₈O₃ (128.124): C, 56.24; H, 6.29. Found: C, 55.98; H, 6.25.

**4-Ethyl-4-methyl-5-methylene-1,3-dioxolan-2-one (b):** colorless liquid (2.75 g, 97%) distilled under reduced pressure (12 mmHg, bp 82–84 °C); δ_H (400 MHz, CD₃COCD₃) 4.82 (1H, d, J = 4.0 Hz), 4.52 (1H, d, J = 3.6 Hz), 1.91 (2H, m), 1.63 (3H, s), 0.94 (3H, t, J = 7.6 Hz); ν/cm⁻¹ 1830 (C=O) and 1687 (C=C). GC–MS m/z = 142 (M⁺), 113, 97, 83, 70, 56, 41. Anal. Calcd for C₇H₁₀O₃ (142.15): C, 59.14; H, 7.09. Found: C, 59.25; H, 6.94.

**4-Isobutyl-4-methyl-5-methylene-1,3-dioxolan-2-one (c):** colorless liquid (3.20 g, 94%) distilled under reduced pressure (12 mmHg, bp 97–100 °C); δ_H (400 MHz, CD₃COCD₃) 4.80 (1H, d, J = 4.8 Hz), 4.55 (1H, d, J = 4.8 Hz), 1.83 (3H, m), 1.63 (3H, s), 0.96 (6H, d, J = 6.0 Hz); ν/cm⁻¹ 1828 (C=O) and 1686 (C=C). GC–MS m/z = 170 (M⁺), 111, 84, 69, 55, 43. Anal. Calcd for C₉H₁₄O₃ (170.20): C, 63.51; H, 8.29. Found: C, 63.25; H, 8.37.

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**Supporting Information Available:** Synthesis and ¹H NMR characterization of ionic liquids and ¹H NMR and IR spectra of compounds a–c (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.