Supporting information

A Recyclable AgI/OAc\textsuperscript{-} Catalytic System for the Efficient Synthesis of \(\alpha\)-Alkylidene Cyclic Carbonates: Carbon Dioxide Conversion at Atmospheric Pressure

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This file includes:

1. General information
2. Experimental section
3. Investigations about the activation mechanism
4. Characterization of products
1. General information

All the compounds involved including the substrates, silver salts and ionic liquids were commercially purchased from Sigma-Aldrich, Aladdin, TCI, Alfa, Macklin in China and used without further dryness and purification. The purity of CO\textsubscript{2} used for purging and reacting was 99.999%. NMR spectra were recorded on a Bruker 500 MHz NMR (\textsuperscript{1}H NMR, 500 MHz; \textsuperscript{13}C NMR, 126 MHz) spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for \textsuperscript{1}H NMR and against the solvent (CDCl\textsubscript{3}, 77.0 ppm; DMSO-\textit{d}_6, 39.9 ppm) for \textsuperscript{13}C NMR, respectively. Multiplicity abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The coupling constants, \textit{J}, were reported in Hertz (Hz).

2. Experimental section

2.1 Synthesis of \(\alpha\)-alkylidene cyclic carbonates by carboxylative cyclization of propargylic alcohols with CO\textsubscript{2} catalyzed by AgI/IL\textsubscript{1} system.

AgI (11.7 mg, 0.05 mmol, 1 mol%), IL\textsubscript{1} (1 mL, 1.102 g, 6.474 mmol), a propargylic alcohol (5 mmol) were added to a Schlenk tube equipped with a magnetic stirring bar. The system was quickly purged 3 times with CO\textsubscript{2}. Then the mixture was stirred at 45 °C, 1 bar of CO\textsubscript{2} for the required time. Upon completion, the mixture was extracted with hexane (4 \times 15 mL). The upper layer was combined and the solvent was removed to obtain the crude product, which could be further purified by column chromatography on silica gel using petroleum ether/ethyl acetate (100:1-20:1) as an eluent. When the reusability of the catalytic system was investigated, the lower layer (recovered IL\textsubscript{1} + AgI) was dried under vacuum for 10-15 minutes to evaporate the residual hexane. After dryness, the recovered IL\textsubscript{1} and AgI were directly reused as the catalyst for the next round.

2.2 NMR yield calculation for the reaction system of CO\textsubscript{2} with propargylic alcohols.

The \textsuperscript{1}H NMR spectra of the crude reaction mixture generated by 2-methylbut-3-yn-2-ol and CO\textsubscript{2} (Figure S1) was used as an example for the quantitative determination of products employing 1,1,2,2-tetrachloroethane as the internal standard. The deuterated solvent is CDCl\textsubscript{3}.

Two protons that belongs to the double bonds of \(\alpha\)-alkylidene cyclic carbonates (red and green marked), which are far away from the alkyl and aryl protons and show two clear individual peaks, could be treated as characteristic protons for quantitative determination. The sharp peak at \(\delta = 5.98\) ppm (blue marked) represents two protons of 1,1,2,2-tetrachloroethane. Therefore, the exact amount and the NMR yield of the product could be calculated by the ratio of double bond proton and internal standard proton based on the exact amounts of 1,1,2,2-tetrachloroethane and the substrate.
Example: is = internal standard, p = product, s = substrate.

\[ m(\text{is}) = 0.8668 \text{ g}, \quad M(\text{is}) = 167.86 \text{ g/mol}. \]
\[ n(\text{is}) = 5.164 \text{ mmol}. \]

\[ \text{ratio (is/p)} = 2.23/2 : 1 = 1.115. \]
\[ n(\text{p}) = n(\text{is}) / \text{ratio (is/p)} = 4.631 \text{ mmol}. \]

\[ m(s) = 0.4187 \text{ g}, \quad M(s) = 84.12 \text{ g/mol}. \]
\[ n(s) = 4.977 \text{ mmol}. \]

Therefore, NMR yield = \( n(\text{p}) / n(s) = 93\% \).

Figure S1. \( ^1\text{H} \) NMR of crude product generated by 2-methylbut-3-yn-2-ol and CO\(_2\).

2.3 The isolated yields of 2a-2h

Table S1. The isolated yields of 2a-2h.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Time</th>
<th>Yield(^b)</th>
<th>Yield(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td><img src="https://example.com/structure" alt="Structure" /></td>
<td>2a</td>
<td>3 h</td>
<td>93%</td>
</tr>
</tbody>
</table>
1b  \[
\begin{align*}
&\text{OH}^+ \\
\end{align*}
\]  $\rightarrow$  \[
\begin{align*}
&\text{O}^+ \\
\end{align*}
\]  $\text{O}$  \[
\begin{align*}
&\text{4 h} \\
\end{align*}
\]  $96\%$  $93\%$

1c  \[
\begin{align*}
&\text{OH}^+ \\
\end{align*}
\]  $\rightarrow$  \[
\begin{align*}
&\text{O}^+ \\
\end{align*}
\]  $\text{O}$  \[
\begin{align*}
&\text{3 h} \\
\end{align*}
\]  $91\%$  $87\%$

1d  \[
\begin{align*}
&\text{OH}^+ \\
\end{align*}
\]  $\rightarrow$  \[
\begin{align*}
&\text{O}^+ \\
\end{align*}
\]  $\text{O}$  \[
\begin{align*}
&\text{6 h} \\
\end{align*}
\]  $99\%$  $94\%$

1e  \[
\begin{align*}
&\text{OH}^+ \\
\end{align*}
\]  $\rightarrow$  \[
\begin{align*}
&\text{O}^+ \\
\end{align*}
\]  $\text{O}$  \[
\begin{align*}
&\text{8 h} \\
\end{align*}
\]  $88\%$  $83\%$

1f  \[
\begin{align*}
&\text{OH}^+ \\
\end{align*}
\]  $\rightarrow$  \[
\begin{align*}
&\text{O}^+ \\
\end{align*}
\]  $\text{O}$  \[
\begin{align*}
&\text{6 h} \\
\end{align*}
\]  $99\%$  $95\%$

1g  \[
\begin{align*}
&\text{OH}^+ \\
\end{align*}
\]  $\rightarrow$  \[
\begin{align*}
&\text{O}^+ \\
\end{align*}
\]  $\text{O}$  \[
\begin{align*}
&\text{6 h} \\
\end{align*}
\]  $97\%$  $93\%$

1h  \[
\begin{align*}
&\text{Ph}^+ \\
\end{align*}
\]  $\rightarrow$  \[
\begin{align*}
&\text{Ph}^+ \\
\end{align*}
\]  $\text{Ph}$  \[
\begin{align*}
&\text{12 h} \\
\end{align*}
\]  $44\%$  $40\%$

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*a* Reaction conditions: AgI (0.05 mmol), IL$_1$ (1 mL, 1.102 g, 6.474 mmol), substrate (5 mmol), CO$_2$ (1 bar) at 45°C.

*b* NMR Yields were determined by $^1$H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard.

*c* Isolated yields

### 2.4 The mass and the amount of ILs of Table 1.

**Table S2.** The mass and the amount of ILs of Table 1

<table>
<thead>
<tr>
<th></th>
<th>V</th>
<th>m</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL$_1$</td>
<td>1 mL</td>
<td>1.102 g</td>
<td>6.474 mmol</td>
</tr>
<tr>
<td>IL$_2$</td>
<td>1 mL</td>
<td>1.243 g</td>
<td>6.270 mmol</td>
</tr>
<tr>
<td>IL$_3$</td>
<td>1 mL</td>
<td>1.28 g</td>
<td>6.466 mmol</td>
</tr>
<tr>
<td>IL$_4$</td>
<td>1 mL</td>
<td>1.5 g</td>
<td>3.833 mmol</td>
</tr>
<tr>
<td>IL$_5$</td>
<td>/</td>
<td>1.5 g</td>
<td>6.301 mmol</td>
</tr>
</tbody>
</table>
2.5 Comparison of AgI/IL\textsubscript{1} system (this work) with the previously reported reusable silver systems.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Year</th>
<th>Authors</th>
<th>Catalytic systems</th>
<th>General reaction condition</th>
<th>CO\textsubscript{2} pressure</th>
<th>Recycle rounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2013</td>
<td>Yuan et al.</td>
<td>Polystyrene-supported -NHC-Ag</td>
<td>2 mol% of Polystyrene - supported-NHC-Ag</td>
<td>5 MPa</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>2014</td>
<td>He et al.</td>
<td>Ag\textsubscript{2}WO\textsubscript{4} PPh\textsubscript{3}</td>
<td>1 mol% of Ag\textsubscript{2}WO\textsubscript{4} 2 mol% of PPh\textsubscript{3}</td>
<td>0.1 MPa</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>2014</td>
<td>Liu et al.</td>
<td>Fluorinated-MOP-Ag DBU</td>
<td>10 mol% of Ag 1 equiv of DBU</td>
<td>1 MPa</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>2015</td>
<td>Han et al.</td>
<td>Ag nanoparticles-sulfonated macrorietical resin DBU</td>
<td>10 mol% of Ag 1 equiv of DBU</td>
<td>0.1 MPa</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>2015</td>
<td>He et al.</td>
<td>[(Ph\textsubscript{3}P)\textsubscript{2}Ag\textsubscript{2}]CO\textsubscript{3}</td>
<td>1 mol% of [(Ph\textsubscript{3}P)\textsubscript{2}Ag\textsubscript{2}]CO\textsubscript{3}</td>
<td>0.1 MPa</td>
<td>&gt;2</td>
</tr>
<tr>
<td>6</td>
<td>2016</td>
<td>Wang et al.</td>
<td>AgOAc [P\textsubscript{66614}][DEIm]</td>
<td>1 mol% of AgOAc 10 mol% of [P\textsubscript{66614}][DEIm]</td>
<td>0.1 MPa</td>
<td>&gt;5</td>
</tr>
<tr>
<td>7</td>
<td>2016</td>
<td>Liu et al.</td>
<td>poly(PPh\textsubscript{3})-azo-Ag DBU</td>
<td>0.064 mol% of Ag 1 equiv of DBU</td>
<td>1 MPa</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>2016</td>
<td>Wang et al.</td>
<td>AgI@C DBU</td>
<td>3 mol% of Ag 20 mol% of DBU</td>
<td>0.1 MPa</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>This Work</td>
<td>AgI IL\textsubscript{1}</td>
<td>1 mol% of Ag 1.3 equiv of IL\textsubscript{1}</td>
<td>0.1 MPa</td>
<td>20</td>
</tr>
</tbody>
</table>

3. Investigations about the activation mechanism

In this investigation, all the \textsuperscript{1}H NMR spectra applied were performed in DMSO-\textit{d}_6.

It has been reported that the activation of the hydroxyl proton of the substrate was the pivotal process to initiate the catalytic cycle, which could be monitored by \textsuperscript{1}H NMR.\textsuperscript{1}

Consequently, in order to recognize the species that activated the hydroxyl proton, substrate 1\textit{a} (5 mmol), and the mixture of 1\textit{a}/AgI (5 mmol of 1\textit{a}, 0.05 mmol of AgI), 1\textit{a}/IL\textsubscript{1} (5 mmol of 1\textit{a}, 1 mL of IL\textsubscript{1}) were respectively added to a Schlenk tube and directly analyzed by \textsuperscript{1}H NMR. The obtained spectra were supplied in Figure S2.

In Figure S2(a), a peak at $\delta = 5.29$ ppm was considered as the hydroxyl proton of
the substrate. When AgI was added into 1a, no significant difference was observed, indicating that AgI individually couldn’t activate the hydroxyl proton. Nevertheless, when IL1 was mixed with 1a, the peak of hydroxyl proton was extremely extended as a quite board peak at $\delta = 6.45$ ppm (Figure S3). These results implied that the activation was accomplished by the IL component of the catalytic system.

Figure S2. $^1$H NMR of (a) pure 1a in DMSO-$d_6$, (b) AgI+1a in DMSO-$d_6$, (c) IL1+1a in DMSO-$d_6$, (d) pure IL1 in DMSO-$d_6$

Figure S3. $^1$H NMR of IL1+1a in DMSO-$d_6$ (peaks marked with chemical shifts belong to 1a)

4. Characterization of products
4, 4-Dimethyl-5-methylene-[1,3]dioxolan-2-one (2a)
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 4.77 (d, $J = 4.0$ Hz, 1H), 4.33 (d, $J = 4.0$ Hz, 1H), 1.62 (s, 6H).
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 158.74, 151.27, 85.30, 84.65, 27.56.
The spectroscopic data matched those reported in the literature.$^9$

4-Ethyl-4-methyl-5-methylene-[1,3]dioxolan-2-one (2b)
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 4.83 (d, $J = 4.0$ Hz, 1H), 4.28 (d, $J = 3.9$ Hz, 1H), 1.93 (dq, $J = 14.6$ Hz, 7.4 Hz, 1H), 1.78 (dq, $J = 14.7$ Hz, 7.4 Hz, 1H), 1.60 (s, 3H), 1.01 (t, $J = 7.4$ Hz, 3H).
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 157.48, 151.53, 87.56, 85.53, 33.40, 25.95, 7.32.
The spectroscopic data matched those reported in the literature.$^9$

4, 4-Diethyl-5-methylene-[1,3]dioxolan-2-one (2c)
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 4.88 (d, $J = 3.8$ Hz, 1H), 4.24 (d, $J = 3.9$ Hz, 1H), 1.95 (dq, $J = 14.6$ Hz, 7.3 Hz, 2H), 1.72 (dt, $J = 14.8$ Hz, 7.4 Hz, 2H), 0.99 (t, $J = 7.4$ Hz, 6H).
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 155.83, 151.85, 90.83, 85.78, 31.90, 7.10.
The spectroscopic data matched those reported in the literature.$^9$
4-Isobutyl-4-methyl-5-methylene-[1, 3] dioxolan-2-one (2d)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 4.81 (d, $J$ = 3.9 Hz, 1H), 4.29 (d, $J$ = 3.9 Hz, 1H), 1.90 – 1.80 (m, 2H), 1.70 – 1.66 (m, 1H), 1.60 (s, 3H), 1.00 – 0.98 (m, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 158.37, 151.45, 87.30, 85.54, 48.57, 27.02, 24.29, 23.98, 23.68.

The spectroscopic data matched those reported in the literature.$^9$

4-Methylene-1, 3-dioxa-spiro [4.4] nonan-2-one (2e)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 4.81 (d, $J$ = 3.9 Hz, 1H), 4.36 (d, $J$ = 3.9 Hz, 1H), 2.28 – 2.23 (m, 2H), 1.98 – 1.83 (m, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 157.79, 151.46, 94.21, 85.31, 40.65, 24.25.

The spectroscopic data matched those reported in the literature.$^5$

4-Methylene-1, 3-dioxa-spiro [4.5] decan-2-one (2f)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 4.78 (d, $J$ = 3.8 Hz, 1H), 4.30 (d, $J$ = 3.8 Hz, 1H), 2.04 – 2.02 (m, 2H), 1.79 – 1.59 (m, 7H), 1.38 – 1.28 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 158.79, 151.46, 86.38, 85.46, 37.53, 24.37, 21.62.

The spectroscopic data matched those reported in the literature.$^9$
4-Isopropyl-4-methyl-5-methylene-1, 3-dioxolan-2-one (2g)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 4.84 (d, $J = 3.8$ Hz, 1H), 4.28 (d, $J = 3.8$ Hz, 1H), 1.99-1.93 (m, 1H), 1.59 (s, 3H), 1.03 (dd, $J = 13.4$ Hz, 13.4 Hz, 6H).
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 157.14, 151.71, 89.82, 86.21, 36.99, 24.04, 16.34, 16.04.
The spectroscopic data matched those reported in the literature.$^5$

4-Methyl-5-methylene-4-phenyl-1, 3-dioxolan-2-one (2h)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 7.51 – 7.50 (m, 2H), 7.47 – 7.40 (m, 3H), 4.98 (d, $J = 4.0$ Hz, 1H), 4.49 (d, $J = 4.0$ Hz, 1H), 2.00 (s, 3H)
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 157.49, 151.16, 139.30, 129.19, 128.93, 124.70, 88.16, 87.16, 27.47
The spectroscopic data matched those reported in the literature.$^5$
$^{13}$C NMR
$^{1}H$ NMR
$^{13}$C NMR
$^{1}$H NMR

2d

ppm
$^{13}$C NMR

![Carbon-13 NMR spectrum with labeled peaks at 15.8, 15.1, 45, 65.5, 67, 77.2, 71.3, 76.7, 48.5, 27.0, 24.2, 23.9, and 23.6 ppm. The spectrum shows a molecule labeled as 2d.](image-url)
$^1$H NMR

![Diagram of molecular structure](image)

- 1.00 ppm (1H)
- 4.80 ppm (1H)
- 4.35 ppm (1H)
- 2.04 ppm (2H)
- 6.13 ppm (2H)
$^1$H NMR
$^{13}$C NMR

![NMR Spectrum with Chemical Structure](image)

The spectrum shows multiple peaks at various ppm values, indicating the presence of different carbon atoms in the compound. The chemical structure image at the bottom left represents the molecule under study.
References: