Supplementary Material

Carbon Dioxide Utilisation for the Synthesis of Unsymmetrical Dialkyl and Cyclic Carbonates

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A. Procedure for the synthesis of 1d

(5-Diisopropylamino-3-oxapentyl)dimethylethylammonium bis{(trifluoromethyl)sulfonyl}imide \([\text{Pr}_2\text{N(CH}_2\text{)}_2\text{O(CH}_2\text{)}_2\text{N}_1\text{12}][\text{NTf}_2]\) (1b), (8-diisopropylamino-3,6-dioxaoctyl) dimethyl ethyl ammonium bis{(trifluoromethyl)sulfonyl}imide \([\text{Pr}_2\text{N(CH}_2\text{)}_2\text{(OCH}_2\text{CH}_2\text{)}_2\text{N}_1\text{12}][\text{NTf}_2]\) (1c) were prepared in three steps starting with 2-dimethylaminoethanol and 2-[2-dimethylaminoethoxy] ethanol according to the previously published report.\(^1\)

\[
\begin{align*}
\text{N} & \text{O} \hspace{1cm} \text{O} \\
\text{CH}_3\text{CN} & \hspace{1cm} \text{EtBr} \\
\text{Br} & \hspace{1cm} \text{SOCl}_2 \\
\text{NH} & \hspace{1cm} \text{LiNTf}_2 \\
\end{align*}
\]

Scheme 1. Synthesis of ionic liquid 1d

(5-Hydroxy-3-oxapentyl)dimethylethylammonium bromide (3).

2-[2-dimethylamino ethoxy] ethanol (5.34 g, 40.0 mmol) and bromoethane (10.9 g, 100 mmol) were heated under reflux in CH$_3$CN (20.0 mL) for 30 h. After evaporation of the solvent and excess bromoethane in \textit{vacuo} at 60°C, a pale yellow powder was obtained (8.71 g, 90% yield). \(^1\)H-NMR (CD$_3$OD): \(\delta = 3.99\text{-}3.88 \text{ (m, 2H)}, 3.74\text{-}3.66 \text{ (m, 4H)}\), 3.53 (q, \(J = 7.3\), 2H), 1.44-1.34 (m, 3H); \(^1^3\)C-NMR (CD$_3$OD): \(\delta = 73.8, 65.7, 64.2, 62.3, 62.0, 51.7, 8.66\). HRMS-ESI (m/z) calcld for C$_8$H$_{20}$NO$_2$ [M-Br]$^+$ 162.1494, 163.1526, found 162.1228, 163.1431, calcld for [Br]$^-$ 78.9183, 80.9163, found 78.9174, 80.9157.
(5-Chloro-3-oxapentyl)dimethylethylammonium bromide (4).

SOCl₂ (8.55g, 70.0 mmol) was added dropwise at 0°C to a round-bottom flask containing 3 (8.35 g, 34.4 mmol). The system was stirred for 30 min at 0°C and then kept stirring for 6 h at 80°C. After cooling to room temperature, the excess SOCl₂ was removed under reduced pressure. The product was dried in vacuo at 60 °C for 24 h, a brown red liquid was obtained (8.78 g, 98% yield). ¹H-NMR (CD₃OD): δ = 3.99-3.88 (m, 2H), 3.74-3.66 (m, 2H), 3.64-3.57 (m, 4H), 3.53 (q, J = 7.3, 2H), 1.44-1.34 (m, 3H); ¹³C-NMR (CD₃OD): δ = 73.8, 65.7, 64.2, 62.3, 62.0, 51.7, 8.66. HRMS-ESI (m/z) calcd for C₈H₁₉ClNO [M-Br]⁺ 80.1155, 181.1187, 182.1127, found 80.1081, 181.1138, 182.1070, calcd for [Br⁻] 78.9183, 80.9163, found 78.9174, 80.9157.

{5-(1,1,3,3-tetramethylguanidyl)-3-oxapentyl)} dimethylethylammonium bromide hydrochloride (5).

In a constant pressure dropping funnel, 4 (5.20 g, 20.0 mmol) and CH₃OH (6.00 mL) were introduced. This solution was added dropwise at 0 °C to a round-bottom flask equipped with a dry nitrogen inlet containing a solution of TMG (2.30 g, 20.0 mmol) in CH₃OH (6.00 mL). The system was stirred overnight at room temperature. The solvent was evaporated and the residue was further dried under vacuum (40 °C, 24 h) to yield a yellow solid (7.35 g, 98%). ¹H-NMR (CD₃OD): δ = 3.89-3.82 (m, 2H), 3.73-3.59 (m, 4H), 3.50 (dd, J = 5.7, 3.6, 2H), 3.42 (q, J = 7.3, 2H), 3.05 (s, 6H), 2.72 (s, 12H), 1.35-1.24 (m, 3H); ¹³C-NMR (CDCl₃): δ = 161.7, 71.1, 64.9, 62.6, 61.4, 51.3, 50.4, 43.1, 40.3, 8.58. HRMS-ESI (m/z) calcd for C₁₃H₃₂N₄O [M-Br-Cl]⁺ 260.2576, found 260.2639, calcd for [Br⁻] 78.9183, 80.9163, found 78.9165, 80.9143.
{5-(1,1,3,3-tetramethyl guanidyl) -3-oxapentyl)} dimethylethylammonium bromide (6).

\[
\text{N} \quad \text{O} \quad \text{N} \quad \text{N} \quad \text{Br}
\]

Compound 5 (3.75g, 10.0 mmol), NaOH (0.480g, 12.0 mmol) and CH₂Cl₂ 10.0 mL were introduced into a 25 mL round-bottom flask. The system was stirred for 24 h at room temperature. NaOH was isolated by filtration and the filtrate was evaporated on rotary evaporator. The residue was further dried under vacuum (60°C, 24 h) to yield a pale yellow liquid (3.05g, 90%).¹H-NMR (CDCl₃): δ = 4.10-4.01 (m, 2H), 3.93 (dd, J = 5.7, 3.5 2H), 3.87-3.74 (m, 4H), 3.69 (dd, J = 5.7, 4.4, 2H), 3.41 (s, 6H), 2.75 (s, 12H), 1.44 (t, J = 7.2, 3H); ¹³C-NMR (CDCl₃): δ = 167.5, 74.1, 64.8, 62.7, 61.4, 51.4, 43.2, 39.3, 8.67. HRMS-ESI (m/z) calcd for C₁₃H₃₁N₄O [M-Br]⁺ 259.2498, found 259.2561, calcd for [Br]⁻ 78.9183, 80.9163, found 78.9171, 80.9152.

{5-(1,1,3,3-tetramethyl guanidyl) -3-oxapentyl)} dimethylethylammonium bis{(trifluoromethyl)sulfonyl}amide (1d).

\[
\text{N} \quad \text{O} \quad \text{N} \quad \text{NTf₂}
\]

Lithium bis{(trifluoromethyl)sulfonyl} amide (1.58g, 5.50 mmol) in deionised water was added to a solution of 6 (1.70g, 5.00 mmol) in CH₂Cl₂ (20.0 mL). The system was kept stirring for 24 h at room temperature. The CH₂Cl₂ layer was then washed with deionised water several times to remove the salt from the organic phase. After removal of the solvent and drying overnight in high vacuum at 60°C, 1d was obtained as a pale yellow liquid (2.43g, 90%).¹H-NMR (CD₃OD): δ = 4.00-3.89 (m, 2H), 3.78 (dt, J = 5.5, 1.6, 2H), 3.75-3.68 (m 2H), 3.58 (dd, J = 5.6, 3.8, 2H), 3.50 (q, J = 7.3, 2H), 3.14 (s, 6H), 2.98 (s, 12H), 1.38 (ddd, J = 7.3, 5.3, 2.0, 3H); ¹³C-NMR (CD₃OD): δ = 163.3, 126.0, 122.8, 119.7, 116.5, 72.4,
65.5, 64.0, 62.4, 51.7, 44.0, 39.9, 8.54. HRMS-ESI \((m/z)\) calcd for \(\text{C}_{13}\text{H}_{31}\text{N}_{4}\text{O} [2\text{M}+\text{NTf}_2]^+\) 798.4169, found 798.1321, calcd for \(\text{C}_{2}\text{F}_{6}\text{NO}_{4}\text{S}_{2} \ [\text{NTf}_2]^-\) 279.9173, 281.9131, found 279.8868, 281.9073.

**B. Recycling of IL**

For IL recycling, ionic liquid was isolated from the reaction mixture, first, by adding diethyl ether (After the reaction, IL cannot be dissolved in Et²O.) to remove products. Then sufficient Na₂CO₃ was added into the aq. solution to liberate IL. The IL was recycled in the next run without further purification.

**Table 1 Recycle of 1c.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Runs</th>
<th>Amount of ROH, R’X, 1c</th>
<th>Time / h</th>
<th>Yield / %(^B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fresh</td>
<td>1.0, 0.5, 0.6</td>
<td>48</td>
<td>76</td>
</tr>
<tr>
<td>2</td>
<td>1(^st)</td>
<td>1.0, 0.5, 0.6</td>
<td>48</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>2(^nd)</td>
<td>1.0, 0.5, 0.6</td>
<td>48</td>
<td>75</td>
</tr>
</tbody>
</table>

\(^A\) Reaction conditions: CO₂ (1.0 MPa; carried out in a 16 mL stainless-steel autoclave). \(^B\) Yields were determined by \(^1\)H-NMR respect to the amount of benzyl bromide used in the reaction.

**C. Characterization data of product (2a-2h)**

**Benzyl propargyl carbonate (2a).** Colourless liquid; Yield: 76%; \(^1\)H-NMR (CDCl₃): \(\delta = 7.41\text{-}7.32\) (m, 5H, ArH), 5.20 (s, 2H, PhCH₂O-), 4.74 (d, \(J = 2.5\), 2H, -OCH₂-CCH), 2.52 (t, \(J = 2.5\), 1H, -CCH); \(^13\)C-NMR (CDCl₃): \(\delta = 154.54\) (C=O), 134.88 (Ar), 128.67 (Ar), 128.63 (Ar), 128.38 (Ar), 75.72 (CCH), 70.12 (PhCH₂O-), 55.36 (-OCH₂CCH); HRMS-ESI \((m/z)\) calcd for \(\text{C}_{11}\text{H}_{10}\text{O}_{3} [\text{M}+\text{NH}_4]^+\) 208.0974, found 208.0972.

**Benzyl ethyl carbonate (2b).** Colourless liquid; Yield: 84%; \(^1\)H-NMR (CDCl₃): \(\delta = 7.45\text{-}7.28\) (m, 5H, ArH), 5.16 (s, 2H, PhCH₂O-), 4.21 (q, \(J = 7.1\), 2H, CH₃CH₂-), 1.31 (t, \(J = 7.1\), 3H, CH₃CH₂-);
$^{13}$C-NMR (CDCl$_3$): $\delta = 155.14$ (C=O), 135.35 (Ar), 128.59 (Ar), 128.49 (Ar), 128.31 (Ar), 69.44 (PhCH$_2$O-), 64.14 (-OCH$_2$CH$_3$), 14.26 (-OCH$_2$CH$_3$); HRMS-ESI ($m/z$) calcd for C$_{10}$H$_{12}$O$_3$ [M+NH$_4$]$^+$ 198.1130, found 198.1133.

![Allyl benzyl carbonate (2c)](image)

Allyl benzyl carbonate (2c). Colourless liquid; Yield: 81%; $^1$H-NMR (CDCl$_3$): $\delta = 7.44-7.29$ (m, 5H, ArH), 5.93 (ddt, $J = 17.2$, 10.4, 5.8, 1H, -CH=CH$_2$), 5.42-5.22 (m, 2H, -CH=CH$_2$), 5.17 (s, 2H, PhCH$_2$O-), 4.64 (dt, $J = 5.8$, 1.4, 2H, -CH$_2$CH=CH$_2$); $^{13}$C-NMR (CDCl$_3$): $\delta = 154.97$ (C=O), 135.35 (Ar), 131.53 (-CH=CH$_2$), 128.60 (Ar), 128.54 (Ar), 128.33 (Ar), 118.95 (-CH=CH$_2$), 69.66 (PhCH$_2$O-), 68.58 (-OCH$_2$CH=CH$_2$); HRMS-ESI ($m/z$) calcd for C$_{11}$H$_{12}$O$_3$ [M+NH$_4$]$^+$ 210.1130, found 210.1131.

![Dibenzyl carbonate (2d)](image)

Dibenzyl carbonate (2d). Colourless liquid; Yield: 85%; $^1$H-NMR (CDCl$_3$): $\delta = 7.45-7.28$ (m, 10H, ArH), 5.17 (s, 4H, PhCH$_2$O-); $^{13}$C-NMR (CDCl$_3$): $\delta = 155.10$ (C=O), 135.18 (Ar), 128.59 (Ar), 128.55 (Ar), 128.33 (Ar), 69.74 (PhCH$_2$O-); HRMS-ESI ($m/z$) calcd for C$_{15}$H$_{14}$O$_3$ [M+NH$_4$]$^+$ 260.1287, found 260.1279.

![Benzyl phenyl carbonate (2e)](image)

Benzyl phenyl carbonate (2e). White solid; Yield: 83%; $^1$H-NMR (CDCl$_3$): $\delta = 7.47-7.26$ (m, 7H, ArH), 7.02-6.93 (m, 3H, ArH), 5.07 (s, 2H, PhCH$_2$O-); $^{13}$C-NMR (CDCl$_3$): $\delta = 158.80$ (C=O), 137.09 (Ar), 129.48 (Ar), 128.58 (Ar), 127.94 (Ar), 127.48 (Ar), 114.86 (Ar), 69.93 (PhCH$_2$O-); HRMS-ESI ($m/z$) calcd for C$_{14}$H$_{12}$O$_3$ [M+H]$^+$ 229.0865, found 229.0861.
Benzy1 s-butyl carbonate (2f). Colourless liquid; Yield: 67%; $^1$H-NMR (CDCl$_3$): $\delta = 7.47$-$7.28$ (m, 5H, ArH), 5.15 (s, 2H, PhCH$_2$O-), 4.72 (dd, $J = 12.6$, 6.3, 1H, -OCH(\text{CH}_3)\text{CH}_2\text{CH}_3$), 1.73-$1.52$ (m, 2H, -OCH(\text{CH}_3)\text{CH}_2\text{CH}_3$), 1.27 (d, $J = 6.3$, 3H, -OCH(\text{CH}_3)\text{CH}_2\text{CH}_3$), 0.92 (t, $J = 7.5$, 3H, -OCH(\text{CH}_3)\text{CH}_2\text{CH}_3$); $^{13}$C-NMR (CDCl$_3$): $\delta = 154.89$ (C=O), 135.48 (Ar), 128.56 (Ar), 128.42 (Ar), 128.26 (Ar), 76.80 (-OCH(\text{CH}_3)\text{CH}_2\text{CH}_3$), 69.28 (PhCH$_2$O-), 28.76 (-OCH(\text{CH}_3)\text{CH}_2\text{CH}_3$), 19.36 (-OCH(\text{CH}_3)\text{CH}_2\text{CH}_3$), 9.57 (-OCH(\text{CH}_3)\text{CH}_2\text{CH}_3$); HRMS-ESI ($m/z$) calcd for C$_{12}$H$_{16}$O$_3$ [M+\text{NH}_4]^+ 226.1433, found 226.1435.

1, 3-Dioxan-2-one (2h). White solid; Yield: 92%; $^1$H-NMR (CDCl$_3$): $\delta = 4.46$ (t, 4H, -OCH$_2$), 2.15 (dq, $J = 11.5$, 5.7, 2H, -OCH$_2$CH$_2$O-); $^{13}$C-NMR (CDCl$_3$): $\delta = 148.43$ (C=O), 67.90 (CH$_2$O-), 21.77 (-OCH$_2$CH$_2$O-).
D. Copies of $^1$H NMR spectra of benzyl bromide, propargyl alcohol, benzyl propargyl carbonate and reaction mixture.
E. Copies of $^1$H and $^{13}$C NMR spectra of new products

Fig. S1: NMR spectra of (5-Hydroxy-3-oxapentyl)dimethylethylammonium bromide (3).
Fig. S2: NMR spectra of (5-Chloro-3-oxapentyl)dimethylethylammonium bromide (4).

Fig. S3: NMR spectra of {5-(1,1,3,3-tetramethyl guanidyl) -3-oxapentyl)} dimethylethylammonium bromide hydrochloride (5).
Fig. S4: NMR spectra of \{5-(1,1,3,3-tetramethyl guanidyl) -3-oxapentyl\} dimethylethylammonium bromide (6).
Fig. S5: NMR spectra of \{5-(1,1,3,3-tetramethyl guanidyl) -3-oxapentyl\} dimethylethylammonium bis\{(trifluoromethyl)sulfonyl\} amide (1d).
Fig. S6: NMR spectra of benzyl $s$-butyl carbonate (2f).
Reference: