Supporting Information

Organic base/benzyl bromide: an efficient catalytic system for chemical fixation of CO₂ into cyclic carbonates under metal- and solvent-free conditions

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Experimental Section

General information

All starting materials and solvents commercially available were purchased at the highest quality from Sigma-Aldrich or Wako and used as received unless otherwise indicated. Chemical yields refer to the pure isolated substances. \(^1\text{H}\) (500 MHz) and \(^{13}\text{C}\) (125 MHz) NMR spectra were obtained using a Brucker AV-500 (500 MHz) spectrometer. The chemical shifts of the products were reported in ppm with reference to Me\(_4\)Si as the internal standard in CDCl\(_3\) solution. The data were reported in the following order: chemical shift, multiplicity, coupling constants in Hz and integration. Enantiomeric excesses of the carbonates were determined by HPLC analyses with a Daicel Chiralcel OD-3 with detection at 254 nm.
Representative procedure for the Cyclic Carbonate Formation

\[
\text{R} \quad \text{1a - 10a} + \text{1 atm CO}_2 \xrightarrow{5 \text{ mol\% DBU/PhCH}_2\text{Br}} 65^\circ \text{C, Solvent-free} \rightarrow \text{R} \quad \text{1b - 10b}
\]

4-Chloromethyl-[1,3]dioxolan-2-one (4b)

In a 20 mL two-neck flask, epichlorohydrin 4a (6 mmol, 0.555 g), DBU (5 mol\%, 0.046g) and PhCH\textsubscript{2}Br (5 mol\%, 0.051g) were added and stirred at 65 °C for 22 h under an atmosphere of CO\textsubscript{2} (99.999\%, balloon). After completion, the reaction mixture was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.778g (yield: 95.0%).

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): 5.12–5.01 (m, 1H), 4.69–4.55 (m, 1H), 4.48–4.35 (m, 1H), 3.89 (dd, \(J = 12.5, 4.0\) Hz, 1H), 3.77 (dd, \(J = 12.5, 3.5\) Hz, 1H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): 154.8, 74.7, 67.0, 44.6.

Propylene carbonate (1b)

Propylene oxide (1a, 6 mmol, 0.349 g), DBU (5 mol\%, 0.046g) and PhCH\textsubscript{2}Br (5 mol\%, 0.051g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.502 g (yield: 82.0%).

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): 4.92–4.80 (m, 1H), 4.62–4.51 (m, 1H), 4.10–3.95 (m, 1H), 1.55–1.40 (m, 3H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): 155.2, 73.7, 70.7, 19.3.
4-Butyl-1,3-dioxolan-2-one (2b)

1,2-Epoxyhexane (2a, 6 mmol, 0.601 g), DBU (5 mol%, 0.046g) and PhCH₂Br (5 mol%, 0.051g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.735 g (yield: 85%).

¹H NMR (500 MHz, CDCl₃): 4.80−4.65 (m, 1H), 4.60−4.50 (m, 1H), 4.18−4.01 (m, 1H), 1.85−1.62 (m, 2H), 1.55−1.22 (m, 4H), 0.93 (t, J = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): 155.2, 77.2, 69.4, 33.4, 26.4, 22.2, 13.7.

4-Hexyl-1,3-dioxolan-2-one (3b)

1,2-Epoxyoctane (3a, 6 mmol, 0.769 g), DBU (5 mol%, 0.046g) and PhCH₂Br (5 mol%, 0.051g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 3 : 1) to afford the desired cyclic carbonate 0.568 g (yield: 55%).

¹H NMR (500 MHz, CDCl₃): 4.79−4.68 (m, 1H), 4.60−4.50 (m, 1H), 4.18−4.02 (m, 1H), 1.85−1.62 (m, 2H), 1.55−1.21 (m, 8H), 0.89 (t, J = 6.9 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): 155.2, 77.2, 69.4, 33.7, 31.5, 28.7, 24.3, 22.4, 13.9.

4-(But-3-en-1-yl)-1,3-dioxolan-2-one (5b)

1,2-Epoxy-5-hexene (5a, 6 mmol, 0.589 g), DBU (5 mol%, 0.046g) and PhCH₂Br (5 mol%, 0.051g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 3 : 1) to afford the desired cyclic carbonate 0.795 g (yield: 85%).

¹H NMR (500 MHz, CDCl₃): 5.89−5.75 (m, 1H), 5.57−5.47 (m, 1H), 4.85−4.65 (m, 1H), 4.61−4.50 (m, 1H), 4.18−4.01 (m, 1H), 1.85−1.62 (m, 2H), 1.55−1.22 (m, 4H), 0.93 (t, J = 6.9 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): 155.2, 77.2, 69.4, 33.4, 26.4, 22.2, 13.7.
mol%, 0.051g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.691 g (yield: 81%).

\[ \text{^1H NMR (500 MHz, CDCl}_3\text{)}: 5.89-5.63 (m, 1H), 5.18-4.90 (m, 2H), 4.79-4.60 (m, 1H), 4.59-4.42 (m, 1H), 4.15-3.95 (m, 1H), 2.30-2.01 (m, 2H), 1.95-1.65 (m, 2H). \]

\[ \text{^13C NMR (125 MHz, CDCl}_3\text{)}: 155.1, 136.3, 116.0, 76.5, 69.4, 32.8, 28.6. \]

4-Allyloxymethyl-1,3-dioxolan-2-one (6b)

Allyl glycidyl ether (6a, 6 mmol, 0.685 g), DBU (5 mol%, 0.046g) and PhCH\textsubscript{2}Br (5 mol%, 0.051g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.807 g (yield: 85%).

\[ \text{^1H NMR (CDCl}_3\text{, 500 MHz): 5.95-5.80 (m, 1H), 5.35-5.12 (m, 2H), 4.93-4.80 (m, 1H), 4.60-4.45 (m, 1H), 4.44-4.30 (m, 1H), 4.11-3.99 (m, 2H), 3.75-3.65 (m, 1H), 3.64-3.52 (m, 1H). } \]

\[ \text{^13C NMR (125 MHz, CDCl}_3\text{): 155.2, 133.9, 116.0, 76.5, 69.4, 32.8, 28.6. } \]

4-(Phenoxy methyl)-1,3-dioxolan-2-one (7b)

1,2-Epoxy-3-phenoxy propane (7a, 6 mmol, 0.900 g), DBU (5 mol%, 0.046g) and PhCH\textsubscript{2}Br (5 mol%, 0.051g) were combined in a 20 mL two-neck flask according to
the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 1.09 g (yield: 94%).

$^1$H NMR (500 MHz, CDCl$_3$): 7.36–7.22 (m, 2H), 7.06–6.92 (m, 1H), 6.91–6.85 (m, 2H), 5.06–4.95 (m, 1H), 4.65–4.56 (m, 1H), 4.55–4.46 (m, 1H), 4.22 (dd, $J = 10.5$, 4.0 Hz, 1H), 4.12 (dd, $J = 10.5$, 3.5 Hz, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$): 157.8, 154.8, 129.7, 122.0, 114.7, 74.2, 66.9, 66.2.

**4-Phenyl-1,3-dioxolan-2-one (8b)**

In a 20 mL two-neck flask, styrene oxide 8a (6 mmol, 0.721 g), DBU (5 mol%, 0.046g) and PhCH$_2$Br (5 mol%, 0.051g) were added and stirred at 65 °C for 22 h under an atmosphere of CO$_2$ (99.999%, balloon). After completion, the reaction mixture was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.806 g (yield: 82.0%).

$^1$H NMR (500 MHz, CDCl$_3$): 7.42–7.37 (m, 2H), 7.37–7.30 (m, 3H), 5.70–5.60 (m, 1H), 4.81–4.70 (m, 1H), 4.31–4.20 (m, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$): 155.0, 135.9, 129.7, 129.2, 126.0, 78.0, 71.2.

**Hexahydro-benzo[1,3]dioxol-2-one (9b)**

In a 20 mL two-neck flask, styrene oxide 9a (6 mmol, 0.589 g), DBU (5 mol%, 0.046g) and PhCH$_2$Br (5 mol%, 0.051g) were added and stirred at 95 °C for 22 h under an atmosphere of CO$_2$ (99.999%, balloon). After completion, the reaction mixture was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to
afford the desired cyclic carbonate 0.251 g (yield: 31.0%).

$^1$H NMR (300 MHz, CDCl$_3$): 4.76-4.59 (m, 2H), 2.0-1.79 (m, 4H), 1.72-1.53 (m, 2H), 1.51-1.31 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$): 155.35, 75.73, 26.78, 19.17.

(R)-4-Benzylxymethyl-1,3-dioxolan-2-one ((R)-10b)

(R)-Glycidyl benzyl ether (10a, 6 mmol, 0.985 g), DBU (5 mol%, 0.046g) and PhCH$_2$Br (5 mol%, 0.051g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 1.10g (yield: 89%).

$^1$H NMR (500 MHz, CDCl$_3$): 7.40-7.27 (m, 5H), 4.88-4.75 (m, 1H), 4.55 (q, J = 12.0 Hz, 2H), 4.47 (t, J = 8.5 Hz, 1H), 4.37 (dd, J = 8.5 Hz, 6.5 Hz, 1H), 3.71 (dd, J = 10.5 Hz, 3.5 Hz, 1H), 3.61 (dd, J = 11.0 Hz, 3.5 Hz, 1H) $^{13}$C NMR (125 MHz, CDCl$_3$): 154.91, 137.06, 128.59, 128.1, 127.77, 74.98, 73.73, 68.84, 66.31
Reaction of chiral epoxide

(R)-4-Phenyl-1,3-dioxolan-2-one ((R)-8b)

\[
\text{Reaction of } (R)\text{-styrene oxide was conducted according to the representative procedure, and the } ee \text{ of the product was determined by chiral HPLC measurement using Chiralcel OD-3, 10\% IPA/hexanes, 1 mL/min, } t_R = 19.89 \text{ min, } t_S = 24.8 \text{ min, 254 nm. Minimal racemization of the product (98\% } ee \text{) relative to the starting material (99\% } ee \text{) was observed.}
\]

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(R)-4-Benzylxoylmethyl-1,3-dioxolan-2-one ((R)-10b)

Reaction of (R)-Glycidyl benzyl ether was conducted according to the representative procedure, and the ee of the product was determined by chiral HPLC measurement using Chiralcel OD-3, 10% IPA/hexanes, 1 mL/min, t<sub>R</sub>=32.48 min, t<sub>S</sub>=37.64 min, 254 nm. Some racemization of the product (84% ee) relative to the starting material (99% ee) was observed.

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When only DBU was used as catalyst, \((R)-10b\) was obtained in 35% yield with retention of stereochemistry (>99\% ee), and the ee of the product was determined under the same condition.

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$^1$H and $^{13}$C NMR Spectra:
13C with 1H decoupling

2b

ppm

ppm