Selective Production of Cyclic Carbonate over Polycarbonate using Double Metal Cyanide-Quaternary ammonium Salt Catalyst System

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1. Experimental details

1.1 Materials

Zinc chloride (≥98%), potassium hexacyanocobaltate(III) (K$_3$ Co(CN)$_6$), tertiary butyl alcohol (99+%) and Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPGPEG; $M_n = 1,100$) were purchased from Aldrich and used without further purification. All quaternary ammonium salts are kept in a glove box under argon atmosphere and used without further purification. Tetrapropylammonium chloride ($n$Pr$_4$NCl, 98%) and tetrahexylammonium chloride ($n$Hex$_4$NCl, 96%) were obtained from Aldrich. Tetrabutylammonium chloride ($n$Bu$_4$NCl, ≥ 97%), tetraoctylammonium chloride ($n$Oct$_4$NCl, ≥ 97%), tetradecylammonium chloride ($n$Dodec$_4$NCl, ≥ 99%) and tetrabutylammonium bromide ($n$Bu$_4$NBr, ≥ 99%) were purchased from Fluka chemicals. Carbon dioxide of 99.999% purity was used without further purification.

1.2 Catalyst synthesis

The synthetic procedure for the double metal cyanide complexes and its characterizations are well explained in our previous report.$^R$I The catalyst for the present study is denoted as DMC-1.

1.3 General procedure for the cycloaddition reaction

Representative procedure for the cycloaddition reaction is detailed in the manuscript. All cyclic carbonates were isolated by column chromatography and analyzed through FT-IR (IR spectra were recorded on Shimadzu Fourier Transform Infrared spectrometer IRPrestige-21), GC/MS
(Agilent 5975C) and $^1$H-NMR spectroscopy (Varian Gemini 2000, 300 MHz using CDCl$_3$ as solvent).

1.4 Recycling tests

After the reaction the catalyst is removed by filtration and washed with methylene chloride, dried in vacuum for 10 h. The reaction is performed by the previously described procedure. The results are given below.

**Table S-1 Recycling test of DMC catalyst**

<table>
<thead>
<tr>
<th>Recycle</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>Fresh</td>
<td>47.8</td>
<td>47.6</td>
</tr>
<tr>
<td>1</td>
<td>44.9</td>
<td>43.8</td>
</tr>
<tr>
<td>2</td>
<td>44.5</td>
<td>44.1</td>
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<tr>
<td>3</td>
<td>42.0</td>
<td>41.8</td>
</tr>
<tr>
<td>4</td>
<td>40.1</td>
<td>39.8</td>
</tr>
</tbody>
</table>

*Reaction conditions: styrene oxide 1a (20 ml, 184 mmol), Catalyst (40 mg, 0.184 mmol Zn), quaternary salt (2 mmol), time: 2 h, 100 °C CO$_2$ pressure: 0.34 MPa.*
1.4 Product characterization

1. 4-Phenyl-[1,3]dioxolan-2-one (1b): Yield: 94% (GC); 87% (isolated) after purification by column chromatography (hexane / EtOAc 2:3).\textsuperscript{R2}

\begin{center}
\includegraphics[width=0.5\textwidth]{figure_s1}
\end{center}

\textbf{Fig. S1.} $^1$H-NMR spectra of 1b
Fig. S2. FT-IR spectra of 1b

Fig. S3. Mass spectrum of 1b
2. 4-Methyl-[1,3]dioxolan-2-one (2b): Yield: 95% (GC); 90% (isolated) after purification by column chromatography (hexane / EtOAc 4:1). R3

Fig. S4. $^1$H-NMR spectra of 2b
**Fig. S5.** FT-IR spectra of 2b

**Fig. S6.** Mass spectrum of 2b
3. 4-Butyl-[1,3]dioxolan-2-one (3b): Yield: 99% (GC); 95% (isolated) after purification by column chromatography (hexane / EtOAc 2:3).\(^{R2a, R3(a),(b), R4}\)

![Chemical structure of 3b](image)

**Fig. S7.** \(^1\)H-NMR spectra of 3b
Fig. S8. FT-IR spectra of 3b

Fig. S9. Mass spectrum of 3b
4. 4-Chloromethyl-[1,3]dioxolan-2-one(4b): Yield: 95% (GC); 92% (isolated) after purification by column chromatography (hexane / EtOAc 2:3). R2(a),(b); R3b; R4(a),(f),(g); R5

Fig. S10. $^1$H-NMR spectra of 4b
Fig. S11. FT-IR spectra of 4b

Fig. S12. Mass spectrum of 4b
5. 4-Benzyl-[1,3]dioxolan-2-one (5b): Yield: 96% (GC); 93% (isolated) after purification by column chromatography (hexane / EtOAc 2:3).

Fig. S13. $^1$H-NMR spectra of 5b
Fig. S14. FT-IR spectra of 5b

Fig. S15. Mass spectrum of 5b
6. Hexahydro-benzo[1,3]dioxol-2-one(6b): Yield: 75% (GC); 70% (isolated) after purification by column chromatography (hexane / EtOAc 4:1).\textsuperscript{R4(a),(e)}

Fig. S16. $^1$H-NMR spectra of 6b
**Fig. S17.** FT-IR spectra of 6b

**Fig. S18.** Mass spectrum of 6b
References


