Asymmetric Catalysis with CO_2: Direct Synthesis of Optically Active Propylene Carbonate from Racemic Epoxides

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Chemical fixation of CO_2 is of great interest in connection with the development of a truly environmentally benign process, since there are many possibilities for CO_2 to be used as a safe and cheap C_1 building block in organic synthesis.[1] One of the most promising methodologies in this area is the synthesis of five-membered cyclic carbonates via the coupling of CO_2 and epoxides.[2] These carbonates are valuable as precursors for polymeric materials such as poly-carbonates, aprotic polar solvents, pharmaceutical/fine chemical intermediates, and in many biomedical applications.[3] In recent decades, numerous catalyst systems have been developed for this transformation.[4] The preparation of optically pure cyclic carbonates is based on the cyclization of chiral diols with triphosgene[5] or the insertion of CO_2 into chiral epoxides catalyzed by zinc(II)[6a] or palladium(0) complexes.[6b] Also, optically active cyclic carbonates could be obtained by enzyme-mediated enantioselective hydrolysis of racemic cyclic carbonates[7] or asymmetric hydrogenation of 5-methylene-1,3-dioxolan-2-ones catalyzed by chiral ruthenium complexes.[8]

Pursuant to our own efforts toward the development of highly efficient catalysts for coupling CO_2 with epoxides under extremely mild conditions,[9] we became interested in the possibility of developing catalyst systems for direct synthesis of optically active cyclic carbonates from the racemic epoxides, which are inexpensive or easily accessible from inexpensive commercial starting materials. The key to accomplishing this goal is the rational design of improved catalysts based on mechanistic understanding. A general pattern in the coupling of CO_2 with epoxides has emerged wherein catalysis involves activation of both epoxides and CO_2.[4i] Our recent research found that the synergistic actions of an electrophile for epoxide activation in conjunction with a nucleophile for CO_2 activation were more effective in catalyzing this reaction.[9,10] If an electrophile can selectively complex one enantiomer of racemic epoxides, the attack of nucleophile or activated CO_2 to the coordinated epoxide on the less substituted carbon regioselectively will lead to enantioselective ring-opening of epoxides and then further form chiral cyclic carbonates via intramolecular cyclic elimination (Scheme 1). Recently, we noted that chiral SalenCo-(III) complexes (Jacobsen catalyst) had been demonstrated to be a highly efficient and enantioselective catalyst for the hydrolytic kinetic resolution of terminal epoxides.[11] In this system, one SalenCo(III) molecule was proposed to serve as Lewis acid for epoxide activation and another as counterion for the nucleophile. The result stimulated us to design a bifunctional nucleophile– electrophile catalyst system based on chiral SalenCo(III) complexes for directly synthesizing optically pure cyclic carbonates from racemic epoxides. Herein, we describe a convenient route to optically active propylene carbonate by a catalytic kinetic resolution

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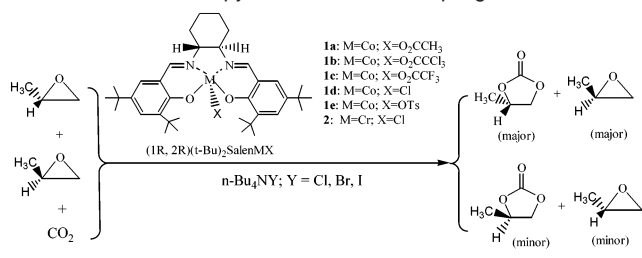‡ Chinese Academy of Sciences.

Scheme 1
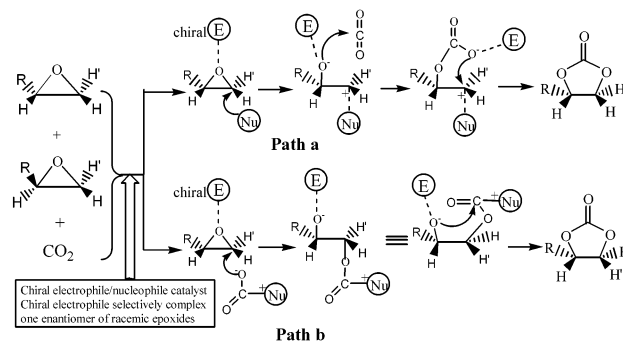
process resulting from the coupling reaction of CO_2 and racemic epoxides using simple chiral SalenCo(III)/quaternary ammonium halide catalyst systems.

Indeed, the exploration of highly efficient catalysts for the coupling reaction of CO_2 and epoxides under low temperature and low CO_2 pressure still remains a challenging problem.[4c,d,12] For example, a recently reported catalyst system is Cr(III)Salen/DMAP, which operates at 25 °C and 100 psig CO_2 pressure, but the formation rate of propylene carbonate is less than 3 h^{-1}.[4k] We delightfully found that the solvent-free reaction of racemic propy-lene oxide (0.5 mol) with 0.55–0.60 equiv of CO_2 in the presence of 0.1 mol % of SalenCo(III)(O_2CCCl_3) complex **1b** using as chiral electrophile in conjunction with 0.1 mol % of n-Bu$_4$NBr as nucleophile proceeded within 2 h at room temperature to afford a mixture of unreacted epoxide and propylene carbonate with moderate enantioselectivity (Table 1, run 2), which could be separated conveniently by simple fractional distillation. The residual chiral SalenCo complex was easily recovered by suspension in methanol and collection by vacuum filtration and could be recycled with no observable loss in activity or enantioselectivity (run 3). The formation rate of propylene carbonate is up to turnover frequency (TOF) of 245 h^{-1}. To the best of our knowledge, the catalytic activity should be the highest for the coupling of CO_2 with terminal epoxides under ambient temperature among the reported catalysts, though organometallic Pd(0) complexes have been demonstrated to be effective in coupling CO_2 with the much higher reactivity of vinyl epoxides under mild conditions.[6b,12a] If only **1b** was used as catalyst (0.1 mol %), no reaction occurred (run 7). The coexistence of a quaternary ammonium salt such as n-Bu$_4$NBr is essential to promote this reaction.

It is interesting that the anion of quaternary ammonium salts in the binary catalyst systems has a great effect on enantiomeric purity and reaction rate (runs 1, 9, and 10). It seems that the use of n-Bu$_4$-NCl was more beneficial for improving enantiomeric purity of the products, but had a pronounced negative effect on the rate. The ratio of n-Bu$_4$NCl to complex **1e** had a significant effect on the

Table 1. Racemic Propylene Oxide/CO$_2$ Coupling Results^a

run	cat	cocat	cocat equiv	time [h]	conv [%]	TOF^b [h^{-1}]	PC ee [%]	K_{rel}^{c}
1	**1a**	n-Bu$_4$NBr	1	2.5	52.4	210	42.9	3.9
2	**1b**	n-Bu$_4$NBr	1	2.0	49.0	245	50.5	4.8
3^d	**1b**	n-Bu$_4$NBr	1	2.0	48.2	241	51.1	4.8
4	**1c**	n-Bu$_4$NBr	1	2.2	51.1	232	46.1	4.3
5	**1d**	n-Bu$_4$NBr	1	4.0	48.2	120	39.8	3.3
6	**1e**	n-Bu$_4$NBr	1	2.5	50.8	203	51.6	5.2
7	**1b**	none	0	10.0	0	0	–	–
8	no	n-Bu$_4$NBr	1	10.0	<0.5	<1	–	–
9	**1a**	n-Bu$_4$NI	1	3.0	48.0	160	37.3	3.0
10	**1a**	n-Bu$_4$NCl	1	5.5	50.0	91	54.3	5.7
11	**1e**	n-Bu$_4$NCl	1	4.0	50.5	126	56.7	6.4
12	**1e**	n-Bu$_4$NCl	2	2.5	46.8	187	57.2	6.0
13	**1e**	n-Bu$_4$NCl	10	2.0	48.1	240	55.9	5.8
14^e	**1e**	n-Bu$_4$NCl	2	1.5	47.4	316	35.2	2.8
15^f	**1e**	n-Bu$_4$NCl	2	6.0	43.9	73	63.5	7.2
16^g	**1e**	n-Bu$_4$NCl	2	15.0	40.0	27	70.2	9.0
17	**2**	n-Bu$_4$NI	1	11.0	48.4	44	2.9	1.1
18^h	**2**	DMAP	1	14.0	2.9	3	–	–

^{a} Reaction was carried out in 35 mL (500 mmol) of neat propylene oxide (PO), cat. (0.5 mmol, 0.001 equiv), CO$_2$ (275–300 mmol, 0.55–0.60 equiv) at 25 °C unless otherwise noted. ^{b} The rate is expressed in terms of turnover frequency [TOF, mol of product (mol of catalyst·h)$^{-1}$]. ^{c} $K_{rel} = \ln[1 - c(1 + ee)]/\ln[1 - c(1 - ee)]$, where c is the conversion and ee is the enantiomeric excess of the resulting propylene carbonate (PC). ^{d} The chiral cobalt complex was recycled. ^{e} 45 °C. ^{f} 15 °C. ^{g} 0 °C. ^{h} Reference 4k.

TOF, rather than enantiomeric purity, even up to 10 equiv (runs 11–13). Axial X-group of chiral SalenCo(III)X complexes also affects enantiomeric purity of the resulted propylene carbonate and propylene oxide. The chiral SalenCo(III)X complexes with a sterically bulk axial X-group, such as p-toluene-sulfonate, are essential for attaining high enantioselectivity in this reaction (runs 1–6). Runs 14–16 show the strong influence of reaction temperature. The decrease of reaction temperature from 45 to 0 °C resulted in TOF from 316 h^{-1} rapidly decreasing to 27 h^{-1} and K_{rel} from 2.8 increasing to 9.0, respectively.

Unfortunately, chiral chromium analogues in conjunction with n-Bu$_4$NI could also catalyze this reaction with good reactivity, but with only 2.9% enantioselectivity (run 17). Very recently, the Darensbourg group reported that chiral SalenCr(III)Cl **2** alone or accompanying N-methyl imidazole was an effective catalyst for the coupling of propylene oxide and CO$_2$ to afford poly(propylene carbonate) as the dominant product at ambient temperature.^{13} However, with n-Bu$_4$NI as cocatalyst, cyclic carbonate is the sole product, even though the convertion of propylene oxide approaches 100%.

In conclusion, a convenient route to optically active cyclic carbonates by a catalytic kinetic resolution process resulting from the coupling reaction of CO$_2$ and racemic epoxides has been discovered by using simple and highly efficient chiral SalenCo-(III)/quaternary ammonium halide catalyst systems. The reaction

was carried out with perfect atom economy under solvent-free and extremely mild conditions. Further optimization of such bifunctional nucleophile−electrophile catalyst systems and exploration into the mechanism are now underway in our laboratory.

Supporting Information Available: Experimental procedures and detailed results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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