

# SnCl<sub>4</sub>-organic base: Highly efficient catalyst system for coupling reaction of CO<sub>2</sub> and epoxides

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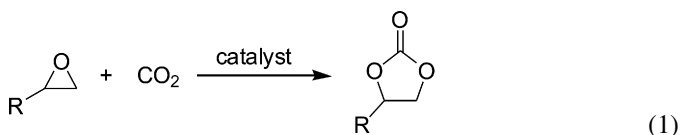
## Abstract

A simple and highly efficient catalyst system of SnCl<sub>4</sub>-organic base was developed to catalyze the coupling reaction of carbon dioxide and epoxides in very mild condition to yield the cyclic carbonates. The proposed mechanism was described in terms of in situ <sup>119</sup>Sn NMR investigations. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Carbon dioxide; Epoxides; Organic base; Stannic chloride; Coupling reaction

## 1. Introduction

Recently, the carbon dioxide fixation has received much attention by reason of carbon dioxide is the most inexpensive and renewable carbon resource from the viewpoint of green chemistry and atom economy [1–5]. The cyclic carbonates are valuable products that are widely used as organic synthetic intermediates, aprotic polar solvents, and raw materials for plastics [6–16]. Various catalyst systems have been developed for the cyclocarbonate synthesis (Eq. (1)) via the coupling reaction of carbon dioxide and epoxides including metal salts, metal oxides, organometallic compounds, ionic liquid, transition-metal and main group complexes [17–30]. Most of these catalysts initiated the coupling reaction under harsh condition.



We have previously reported an efficient catalyst system, SalenSn/DMAP, for coupling reaction of CO<sub>2</sub> and epoxides, that the SalenSn complex and DMAP are not catalysts alone

[31]. The primitive blank experiment of coupling reaction of CO<sub>2</sub> and propylene oxide (PO) was failed due to the insolubility of SnCl<sub>4</sub>-2DMAP precipitates. Surprisingly, when the DMAP was firstly dissolved into PO and then SnCl<sub>4</sub> was added to the solution to make a clearly or little slurry solution, the expected coupling reaction was carried out under very mild condition. We were pleased to discover that the neutral Lewis acid–Lewis base complexes of SnCl<sub>4</sub>-organic base are excellent catalysts for coupling reaction of carbon dioxide and epoxides.

Herein, we disclose our results for the optimization and application of these simple catalysts to various cyclic carbonate syntheses.

## 2. Experimental

### 2.1. Materials

The epoxides were purified and dried with CaH<sub>2</sub>. Stannic chloride and other chemicals were purchased from Aldrich and used without further purification.

### 2.2. General procedure of catalytic coupling reaction

All coupling reactions were performed in a 250 mL glass autoclave, shown clearly the solubility of catalyst, equipped with a magnetic stir bar. The chemicals, dried solvent and autoclave were taken into dry-box. The autoclave was charged successively

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with the epoxide, organic base, and diluting  $\text{SnCl}_4$  (in  $\text{CH}_2\text{Cl}_2$ ). After taking out the closed autoclave from dry-box, it was pressurized with  $\text{CO}_2$  to 100 psi through connecting to the  $\text{CO}_2$  pressure vessel and then was heated and stirred. When the pressure of  $\text{CO}_2$  fell down to 0–15 psi, the reactor was cooled and was then vented. The remaining mixture was distilled under reduced pressure or recrystallized with ethanol to obtain the pure cyclic carbonate.

### 2.3. In situ $^{119}\text{Sn}$ NMR investigations

The investigated samples were prepared by adding  $\text{SnCl}_4$  to  $\text{CH}_2\text{Cl}_2$  in a vial under  $\text{N}_2$  and cooled down in dry ice. It was transferred slowly to another vial containing DBU and PO in toluene (also cooled in dry ice). When the mixture was warmed up to room temperature, it was transferred to an NMR tube to collect the  $^{119}\text{Sn}$  NMR data at  $75^\circ\text{C}$  by using  $\text{Sn}(\text{CH}_3)_4$  as an external standard without lock.

## 3. Results and discussion

### 3.1. Anion effect of catalysts in the coupling reaction of propylene oxide and $\text{CO}_2$

Firstly, different stannic halogenides were used as Lewis acid to form these complex catalysts with two equivalent DMAP (Table 1). The catalytic results demonstrated that  $\text{SnCl}_4$ -2DMAP catalyst has the highest activity comparing with other catalysts.  $\text{SnF}_4$ -2DMAP has no activity due to its insolubility.

### 3.2. Base effect of catalysts in the coupling reaction of propylene oxide and $\text{CO}_2$

Several other organic bases were investigated as possible Lewis base for  $\text{SnCl}_4$ -organic base catalysts (Table 2).  $\text{SnCl}_4$ -DMAP has superior activity in comparison to other organic bases, which might be attributed to its high Lewis basicity.  $\text{SnCl}_4$ -DABCO has no activity at all due to its insolubility. The quantity of organic base was found to be quite important. While the presence of organic base is critical for high activity and the TOF increased upon going from 2 to 5 equivalent of organic base (for DBN, the number is from 2 to 4), further addition of organic base results in a decrease of the TOF.

Finally, extension of these ideas to the different high valency metal chlorides such as the  $\text{ZrCl}_4$ -2DBU and  $\text{SbCl}_5$ -2DBU cat-

Table 2  
The coupling results of  $\text{CO}_2$  and propylene oxide

Entry	Catalyst	Base equivalent	Time (min)	TON	TOF ( $\text{h}^{-1}$ )
1	$\text{SnCl}_4$ -DBU	2	60	552	552
2	$\text{SnCl}_4$ -DBU	3	48	599	749
3	$\text{SnCl}_4$ -DBU	4	36	524	873
4	$\text{SnCl}_4$ -DBU	5	26	420	928
5	$\text{SnCl}_4$ -DBU	6	30	472	944
6	$\text{SnCl}_4$ -DBU	7	30	405	810
7	$\text{SnCl}_4$ -DBN	2	60	444	444
8	$\text{SnCl}_4$ -DBN	3	30	389	778
9	$\text{SnCl}_4$ -DBN	4	30	431	862
10	$\text{SnCl}_4$ -DBN	5	30	366	732
11	$\text{SnCl}_4$ -DBN	6	30	109	219
12	$\text{SnCl}_4$ -DMAP	2	60	535	535
13	$\text{SnCl}_4$ -DMAP	3	35	440	755
14	$\text{SnCl}_4$ -DMAP	4	25	432	1034
15	$\text{SnCl}_4$ -DMAP	5	16	379	1388
16	$\text{SnCl}_4$ -DMAP	6	26	454	1048
17	$\text{SnCl}_4$ -DMAP	7	39	503	774
18	$\text{SnCl}_4$ -Pyridine	5	70	442	379
19	$\text{SnCl}_4$ -Pyridine	4	70	128	109
20	$\text{SnCl}_4$ -NEt <sub>3</sub>	5	300	60	12
21	$\text{SnCl}_4$ -DABCO	5	120	0	0

Reaction condition:  $\text{SnCl}_4$  (26.1 mg, 0.1 mmol), PO (5.8 g, 100 mmol),  $\text{CH}_2\text{Cl}_2$  (0.5 mL),  $T = 75^\circ\text{C}$ ,  $\text{CO}_2$  100 psi.

alyst systems was also investigated in the coupling reaction of PO and carbon dioxide.  $\text{ZrCl}_4$ -2DBU has activity with 102 of TOF value and  $\text{SbCl}_5$ -2DBU shown no activity due to its insolubility. It is worth to mention that the cheap and easy to handle stannic chloride hydrate of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  was also used to make precipitate with five equivalent DBU that can also catalyze efficiently the coupling reaction of PO and carbon dioxide with a little impurity.

### 3.3. The cyclic carbonates syntheses from $\text{CO}_2$ with various epoxides

The  $\text{SnCl}_4$ -5DBU was used as catalyst in the coupling reaction of  $\text{CO}_2$  and various epoxides at  $75^\circ\text{C}$  generating the relevant cyclic carbonates with good to excellent yield (Table 3). This coupling reaction can also take place under more mild condition ( $50^\circ\text{C}$ ) except for the hexene oxide in which the catalyst is insoluble (entry 3). This simple and effective catalyst,  $\text{SnCl}_4$ -5DBU, can also be utilized in the coupling reaction of  $\text{CO}_2$  and cyclohexene oxide (CHO) to conveniently obtain the cyclohexene carbonate under mild condition with high stereoselectivity (94% *cis*-hexahydro-1,3-benzodioxol-2-one, entry 7) [32].

### 3.4. Proposed mechanism of coupling reaction





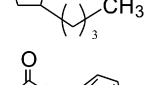
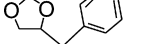
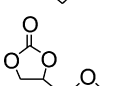

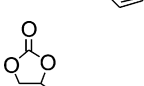
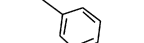


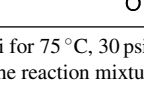
The above results might be explained by considering a similar mechanism for this coupling reaction when using an Cr(III)porphyrin/DMAP catalyst system. In this mechanism (Scheme 1), the epoxides replace the coordinated organic bases to dissolve the precipitate of  $\text{SnCl}_4$ -2Base complexes and be activated by a Lewis acidic metal center,

Table 1  
Anion effect of stannic halogenide/DMAP in the coupling reaction of propylene oxide and  $\text{CO}_2$

Entry	Catalyst	Time (min)	TON	TOF ( $\text{h}^{-1}$ )
1	$\text{SnF}_4$ -2DMAP	300	0	0
2	$\text{SnCl}_4$ -2DMAP	60	535	535
3	$\text{SnBr}_4$ -2DMAP	60	250	250
4	$\text{SnI}_4$ -2DMAP	60	262	262

Reaction condition:  $\text{SnCl}_4$  (26.1 mg, 0.1 mmol), DMAP (24.4 mg, 0.2 mmol), PO (5.8 g, 100 mmol),  $\text{CH}_2\text{Cl}_2$  (0.5 mL),  $T = 75^\circ\text{C}$ ,  $\text{CO}_2$  100 psi.

Table 3  
The coupling results of CO<sub>2</sub> and various epoxides catalyzed by SnCl<sub>4</sub>-5DBU

Entry	Substrate (R=)	Temp. (°C)	Time (h)	Product	Yield (%) <sup>a</sup>
1	CH <sub>3</sub>	75	1.5 <sup>b</sup>		99
		50	3 <sup>b</sup>		100
2	CH <sub>2</sub> Cl	75	1.5 <sup>b</sup>		96
		50	3 <sup>b</sup>		93
3	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	75	2.75		94
		50	5		0
4	Benzyl	75	3		90
		50	5		92
5	PhOCH <sub>2</sub>	75	2		99
		50	6 <sup>c</sup>		66
6	Phenyl	75	1.5		96
		50	4		76
7	Cyclohexane	100	10		78

Reaction conditions: SnCl<sub>4</sub> (26.1 mg, 0.1 mmol), DBU (76 mg, 0.5 mmol), epoxide (50 mmol), CO<sub>2</sub> pressure (50 psi for 75 °C, 30 psi for 50 °C), CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL).

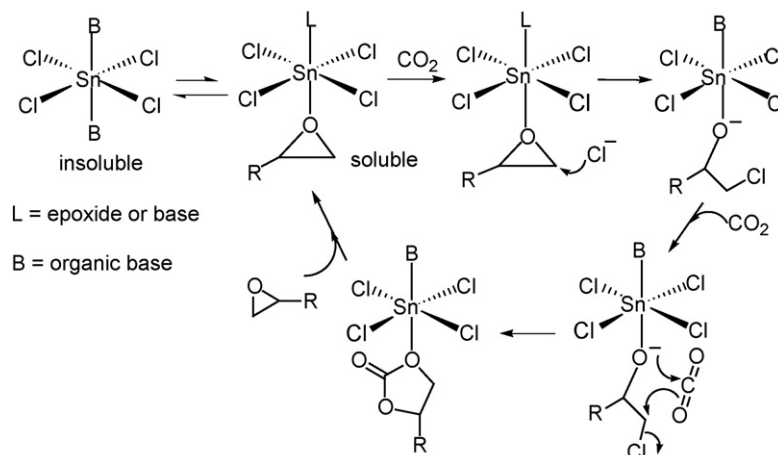
<sup>a</sup> Yield was determined by comparing the ratio of product to substrate in the <sup>1</sup>H NMR spectrum of an aliquot of the reaction mixture.

<sup>b</sup> Epoxide (200 mmol).

<sup>c</sup> Product is solid under this condition.

and then be attacked by nucleophilic reagent to produce the requisite metal alkoxide intermediates suffering insertion of CO<sub>2</sub> to lead cyclic carbonates. The in situ <sup>119</sup>Sn NMR spectra show that there are two peaks for SnCl<sub>4</sub>-4PO (Sn(PO)Cl<sub>4</sub>, -551.8 ppm; Sn(PO)<sub>2</sub>Cl<sub>4</sub>, -555.0 ppm) and six peaks for SnCl<sub>4</sub>-4PO-2DBU (Sn(PO)Cl<sub>4</sub>, -599.5 ppm;

Sn(PO)<sub>2</sub>Cl<sub>4</sub>, -605.2 ppm; Sn(PO)(DBU)Cl<sub>4</sub>, -607.5 ppm; Sn(PO)(POCl)Cl<sub>4</sub>, -630.7 ppm; Sn(POCl)(DBU)Cl<sub>4</sub>, -634.9 ppm; Sn(DBU)<sub>2</sub>Cl<sub>4</sub>, -663.6 ppm) demonstrating different species of the precipitate (insoluble, Sn(DBU)<sub>2</sub>Cl<sub>4</sub>) and the soluble coordinated complexes in the mixture solution comparing one peak for SnCl<sub>4</sub> (-155.9 ppm).



Scheme 1. Proposed mechanism.

#### 4. Conclusion

In summary, we developed a series of novel and high efficient catalysts, SnCl<sub>4</sub>-organic bases. Among them, SnCl<sub>4</sub>-5DBU is one of the best catalysts for the coupling reaction of carbon dioxide and various epoxides yielding relevant cyclic carbonates by which carbon dioxide can be easily introduced into organic molecules under very mild condition.

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