Phenol and Organic Bases Co-Catalyzed Chemical Fixation of Carbon Dioxide with Terminal Epoxides to Form Cyclic Carbonates

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Supporting information for this article is available on the WWW under http://asc.wiley-vch.de or from the author.

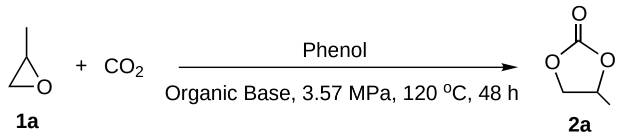
Abstract: Phenol can efficiently catalyze the reactions of terminal epoxides with carbon dioxide in the presence of catalytic amounts of various organic bases such as 4-dimethylaminopyridine (DMAP), pyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene, and triethylamine to give the corresponding five-membered cyclic carbonate in high yields (initial pressure 3.57 MPa; reaction temperature 120 °C). *p*-Methoxyphenol with DMAP is the best combination to give the cyclic carbonate in the highest yield.

Keywords: chemical fixation of carbon dioxide; epoxide; green chemistry; organic base; phenol

Conversion of carbon dioxide to industrially useful compounds has been a challenge for synthetic chemists and has recently attracted much interest in view of the so-called "sustainable society"[1] and "green chemistry"[2] concepts. One of the most attractive synthetic goals starting from carbon dioxide is the five-membered cyclic carbonate system because five-membered cyclic carbonates have many synthetic uses and have generally been synthesized from the corresponding diols and phosgene or related compounds.[3–7] Although many phosgene-free methods to synthesize the corresponding five-membered cyclic carbonates have been reported,[8,9] the reaction of oxirane **1** with carbon dioxide has received much attention because of its simple operation, high yield, and the harmless nature of the reagents. Furthermore, the reaction is one of the most effective methods to incorporate carbon dioxide into organic molecules. In the last decades of the twentieth century numerous catalytic systems have been developed for this transformation. While the advances have been significant,[10–23] all suffer from either low catalyst stability/reactivity, air sensitivity, the need for cosolvent, or catalysts requiring special structures. Herein, we wish to report an extremely simple and eco-safer way to cyclic carbonate from the reactions of epoxide with carbon dioxide in the presence of catalytic amounts of phenol and an organic base.

During our investigations, we found that the five-membered cyclic carbonate **2a** could be obtained in excellent yield from the phenol (0.4 mol %) and an organic base (0.4 mol %) co-catalyzed reactions of epoxides **1** with carbon dioxide under mild conditions (3.57 MPa CO_2, 120 °C, 48 h) (Scheme 1). Using either phenol or the organic base as a sole catalyst, no reaction occurred. The co-existence of phenol and organic base must be required in order to get high yields of cyclic carbonate **2a**. This catalytic system for the chemical fixation of CO_2 is very efficient.

The scope and limitations of catalysts and reaction conditions have been carefully examined. Many phenols (phenol: $pK_a = 10.0$, *m*-nitrophenol: $pK_a = 7.15$, *p*-methoxyphenol: $pK_a = 10.21$, binol: $pK_a = 10.64$, or naphthol: $pK_a = 10.12$) with organic bases (DMAP, DBU, Et_3N, or pyridine) have catalytic abilities for this reaction. The results are summarized in Table 1. 4-Dimethylaminopyridine (DMAP) is the best organic base in this reaction (Table 1, entries 3, 7–10) and *p*-methoxyphenol is the most effective phenol under otherwise the same reaction conditions (Table 1, entries 1–6). These results suggest that both pK_a of the phenol and the structure of the organic base play important roles in this reaction. As the matter of fact, the combination of either alcohol or carboxylic acid with organic base shows no reactivity. We also examined the reaction system using



Scheme 1.

Table 1. Reactions of propylene oxide with CO_2 in the presence of phenol and organic base.[a]

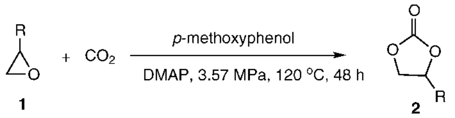
Entry	Phenol	Base	Yield [%][b]	TON[c]
1	PhOH	DMAP	91	228
2	m-$NO_2C_6H_4OH$	DMAP	59	149
3	p-$MeOC_6H_4OH$	DMAP	98	246
4	β-Naphthol	DMAP	90	224
5	Binol	DMAP	94	235
6	8-Hydroxyquinoline	DMAP	55	138
7	p-$MeOC_6H_4OH$	DABCO	13	34
8	p-$MeOC_6H_4OH$	Et_3N	24	61
9	p-$MeOC_6H_4OH$	DBU	69	173
10	p-$MeOC_6H_4OH$	pyridine	20	50

[a] Reaction conditions: propylene oxide (PO) (2.6 g, 45 mmol), CH_2Cl_2 (0.5 mL), phenol (0.18 mmol), organic base (0.18 mmol).

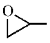
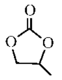
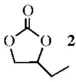
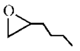
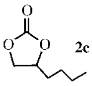
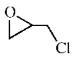
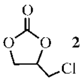
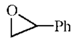
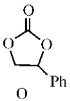
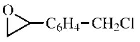
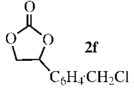
[b] Isolated yield.

[c] Moles of propylene carbonate produced per mole of catalyst.

Table 2. Reactions of epoxide with CO_2 in the presence of p-methoxyphenol and DMAP.[a]



1 **2**

Entry	Epoxide	Product	Yield [%][b]
1		 **2a**	100
2		 **2b**	96
3		 **2c**	94
4		 **2d**	99
5		 **2e**	96
6	 (m- and p-mixture)	 **2f** (m- and p-mixture)	74

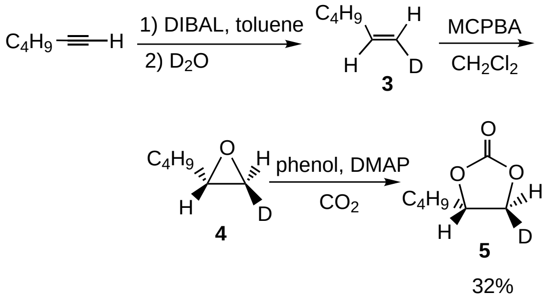
[a] Reaction conditions: epoxides (4.5 mmol), CH_2Cl_2 (0.5 mL), p-methoxyphenol (0.18 mmol), DMAP (0.18 mmol).

[b] Isolated yield.

p-toluenesulfonic acid as a co-catalyst with DMAP, but found that the cyclic carbonate was obtained in only 10% under the same condition for DMAP and phenol. The best combination is p-methoxyphenol (0.4 mol %) with DMAP (0.4 mol %) in this reaction.

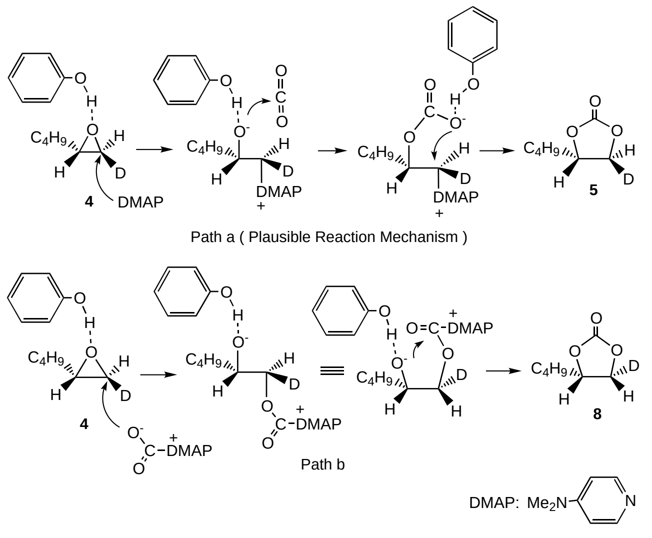
Under the optimized reaction conditions (p-methoxyphenol/DMAP, 3.57 MPa, 120 °C, 48 h), we examined the reactions of other epoxides **1** with carbon dioxide. The results are summarized in Table 2. We found that, by using 4 mol % of p-methoxyphenol and DMAP, many monosubstituted terminal epoxides can be quantitatively transformed to the corresponding cyclic carbonates **2** (Table 2).

Considering the reaction mechanism, Kim showed that in the reaction of epoxide with CO_2 in the presence of $ZnBr_2$ and pyridine, the epoxy ring, activated by the Lewis acid $ZnBr_2$, was opened by the pyridine on the basis of the X-ray crystal structure.[16] Then, it further reacted with CO_2 to give the corresponding cyclic carbonate. However, it is also well known that an organic base can activate CO_2 as a Lewis base[24] and the zwitterion $[R_3N^+C(O)O^-]$ can open the aziridinyl ring.[25] In order to clarify the reaction mechanism, we synthesized *trans*-deuterioethylene oxide as shown in Scheme 2 according to the literature (see supporting information) and utilized it as the substrate in the DMAP and phenol co-catalyzed reaction of epoxides with CO_2 (Scheme 2). The deuterated ethylene carbonate formed was analyzed by comparison with authentic samples prepared according to the literature (see supporting information, ^1H NMR). As the result, we found that deuterated ethylene carbonate **5** was exclusively formed (the lower yield compared by analogy with **2c** may be caused by the secondary isotope effect).[26] This result suggests that the formation of cyclic carbonate in our reaction system proceeds *via* path a as shown in Scheme 3, namely, the epoxy ring activated by phenol through hydrogen bonding is first opened by amine (DMAP) and then reacts with CO_2 to give the corresponding deuterated ethylene carbonate **5** because, if the reaction proceeded *via* path b, another deuterated ethylene carbonate **8** having the opposite configuration of deuterium atoms as **5** should be exclusively formed (Scheme 3).



Scheme 2.

Based on the above results, in Scheme 3 path a, we propose the plausible mechanism for this chemical fixation reaction of CO_2. We believe that, in fact, this is a Lewis base amine and Lewis acid phenol (through hydrogen bonding) co-catalyzed reaction system. The Lewis base and Lewis acid work together to open the epoxy ring and then react with CO_2 to give the corresponding cyclic carbonate *via* a ring opening and recyclization process. Previous reports also suggest the



Scheme 3.

parallel requirement of both Lewis base and Lewis acid in the fixation of the CO_2.[4,12,16,21] As the matter of fact, this is a Lewis base and Lewis acid co-catalyzed system. Alcohols have low Lewis acidity which cannot activate CO_2, whereas it is well known that acids will react with organic bases to give a salt. Only phenols (pK_a: 7.0 ~ 10.5) can selectively activate CO_2. *m*-Nitrophenol (pK_a: 7.15) can combine with organic bases to some extent as well because of its higher acidity. Thus, it has the lowest activity for this chemical fixation of CO_2.

In conclusion, we found that cyclic carbonate can be obtained quantitatively at the reaction conditions (3.57 MPa of CO_2 initial pressure; reaction temperature 120 °C) from the reaction of epoxides **1** with carbon dioxide in the presence of catalytic amounts of phenol and an organic base. This is a very efficient non-metal Lewis acid (phenol) and Lewis base (amine) co-catalyzed system and the cyclic carbonates **2** are obtained in excellent yields as the sole products. Moreover, the reaction mechanism has been disclosed in this paper. Efforts are underway to elucidate the further mechanistic details of this reaction and to identify systems enabling a similar carboxylation of other substrates and subsequent transformation thereof.

Experimental Section

Representative Procedure for the Reactions of Epoxides with Carbon Dioxide

A 100 mL stainless pressure reactor was charged with *p*-methoxyphenol (23 mg, 0.18 mmol), propylene oxide (2.6 g, 45 mmol), DMAP (22 mg, 0.18 mmol), and CH_2Cl_2 (0.5 mL). The reaction vessel was placed under a constant pressure (3.57 MPa) of carbon dioxide for 5 min to allow the system to equilibrate and then heated to 120 °C for 48 h. The vessel was then cooled to ambient temperature, the pressure released, and the contents transferred to a 50 mL round-bottom flask. Unreacted substrate and solvent were removed under vacuum, and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 1/4) to give the cyclic carbonate as a colorless liquid.

Acknowledgements

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