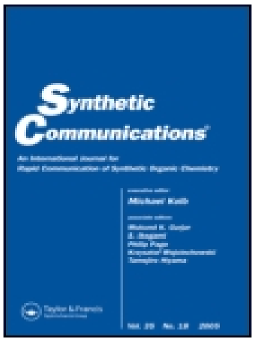

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Convenient synthesis of ethylene carbonates from carbon dioxide and 1,2-diols at atmospheric pressure of carbon dioxide

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ABSTRACT
An efficient and convenient synthesis of ethylene carbonates was achieved by the reaction of carbon dioxide with 1,2-diols in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), followed by treatment with 1-bromobutane. This DBU-promoted transformation proceeded at an atmospheric pressure of carbon dioxide at 25 °C and gave ethylene carbonates in good yields.

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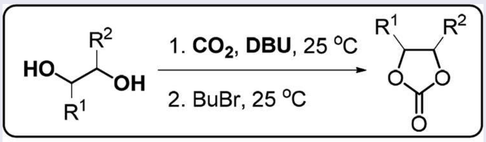
KEYWORDS
Carbon dioxide; 1,2-diols; ethylene carbonates

GRAPHICAL ABSTRACT



One pot synthesis under mild conditions
Atmospheric pressure of CO_2
Good to high yields (up to 95%)

Introduction

Carbon dioxide (CO_2) is a nontoxic and renewable carbon resource that exists abundantly on the earth. However, CO_2 is emitted in the atmosphere by combustion of petroleum, coal, and natural gas, and it causes global warming because of the greenhouse gas effect. Therefore, reduction of CO_2 has become one of the urgent issues in the world. To reduce the amount of CO_2, effective utilization of CO_2 as a carbon source for production of valuable materials is an important subject. The development of such synthetic processes is expected to solve environmental problems and to provide economically valuable materials. Although synthesis of carbonic esters is conducted by using highly toxic phosgene, safer synthetic methods of carbonic esters using CO_2 have been developed in recent years.[1] In the near future, the carbonic ester synthesis using phosgene may be replaced for the method of using CO_2.

On the other hand, ethylene carbonates are also useful materials and the synthesis of cyclic carbonic esters can be efficiently attained by the reaction of CO_2 and oxiranes.[1a,1d,1f,2] Several methods for preparing cyclic carbonates from 1,2-diols and CO_2 have been

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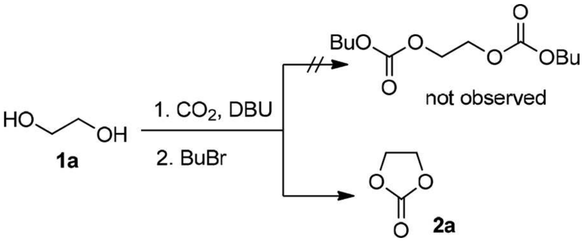
developed.[1a,3] Although 1,2-diols have the advantages of availability and stability, the methods using 1,2-diols are inferior in respect to the yields or the experimental operations compared with the methods using oxiranes. Therefore, the synthesis of ethylene carbonates using 1,2-diols needs improvement in the process.

Previously, it was reported that carbonic esters could be prepared by the capture of carbon dioxide with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) / alcohols, followed by alkylation with an alkyl halide.[4] Because this carbonate synthesis promoted by DBU is convenient and mild, we have attempted to apply it to the synthesis of bis-carbonates from 1,2-diols and CO_2. However, contrary to our expectations, the reaction of ethylene glycol (**1a**) with CO_2 in the presence of DBU followed by alkylation with 1-bromobutane did not give the bis-carbonate of ethylene glycol but ethylene carbonate (**2a**), as shown in Scheme 1. This unexpected result provided us with a new strategy for ethylene carbonate synthesis. Although the formation of ethylene carbonates from 1,2-diols and CO_2 was reported,[5] there are still some drawbacks that should be solved. This procedure requires high pressure of CO_2 (10 bar), heating at 70 °C, addition of expensive ionic liquids, and use of dibromomethane as solvent. Because the reaction under the atmospheric pressure conditions of CO_2 can avoid dangerous high-pressure conditions, it is important for conducting a safe and convenient synthetic reaction. Here we report for the first time an efficient and convenient synthesis of cyclic carbonates from 1,2-diols and CO_2 at atmospheric pressure of CO_2.

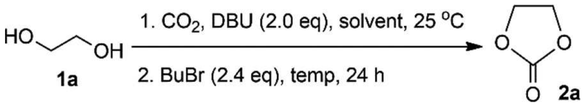
Results and discussion

First, we examined the reaction of ethylene glycol (**1a**) and CO_2, affording ethylene carbonate (**2a**). The reaction was conducted by introducing CO_2 gas into a solution of **1a** in CH_2Cl_2 in the presence of 2 equivalents of DBU, followed by addition of 2.4 equivalents of 1-bromobutane. The reaction mixture was stirred at room temperature for 24 h under CO_2 atmosphere using a balloon. After passing through a short column of silica gel with CH_2Cl_2 to remove the resulting DBU salts, the product mixture was separated by column chromatography on silica gel, giving ethylene carbonate (**2a**) and dibutyl carbonate (**3**) in 95 and 98% yields, respectively (Table 1, entry 1). Elevation of the reaction temperature to 40 or 50 °C decreased the yield of ethylene carbonate to 64 or 45%, respectively (entries 2 and 3). It is considered that the yield of ethylene carbonate decreases due to decarboxylation as the reaction temperature increases. When the reaction was conducted in toluene or acetonitrile as solvent, the yield was decreased (entries 4 and 5). Moreover, trimethylamine (TEA) was used as base instead of DBU, but the reaction did not occur at all (entry 6).



Scheme 1. Unexpected results of reaction from CO_2 and ethylene glycol.

Table 1. Synthesis of ethylene carbonate from ethylene glycol and CO_2.[a]



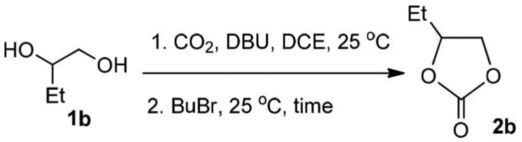
Entry	Solvent	Temperature (°C)	Yield (%)[b]
1	CH_2Cl_2	25	95[c]
2	CH_2Cl_2	40	64
3	CH_2Cl_2	50	45
4	Toluene	25	0
5	MeCN	25	62
6[d]	CH_2Cl_2	25	0

[a] Conditions: **1a** (5 mmol), DBU (10 mmol), BuBr (12 mmol), and solvent (2 mL) at 25 °C.
[b] Yields were determined by ^1H NMR.
[c] Dibutyl carbonate was also formed in 98% yield.
[d] TEA was used instead of DBU.

Next, we examined the reaction using 1,2-butanediol (**1b**) as the substrate bearing a substituent. Because 1,2-butanediol has a less acidic secondary OH group, the reaction conditions needed to optimize again. When the reaction of **1b** was conducted in 1,2-dichloroethane (DCE) using 4.0 equivalents of DBU and 4.8 equivalents of 1-bromobutane, 3-ethylethylene carbonate (**2b**) was formed in 63% yield (Table 2, entry 1). Extension of the reaction time to 48 h did not give a better yield of **2b** (entry 2). Increasing the amount of 1-bromobutane to 9.6 equivalents slightly improved the yield to 67% (entry 3). Finally, we found that the yield of **2b** increased with increasing the amount of DBU (entries 4 and 5). The best yield (96%) of **2b** was obtained when 8 equivalents of DBU were used (entry 5).

With the optimized conditions of 3-ethylethylene carbonate synthesis in hand, we examined the reaction of various 1,2-diols **1** bearing substituents in order to find the scope of the reaction. The results are given in Table 3. When 1,2-propanediol (**1c**) was subjected to the similar reaction conditions to the reaction of 1,2-butanediol (**1b**), 3-methylethylene carbonate (**2c**) was formed in 90% yield (entry 1). Styrenediol (**1d**), 4-(methylphenyl)ethanediol (**1e**), 4-(chlorophenyl)ethanediol (**1f**), and naphthylethanediol (**1 g**) underwent efficiently the transformation to cyclic carbonates, giving the corresponding ethylene carbonates **2** in 84–89% yields (entries 2–5). These reactions suggest that the cyclic carbonate

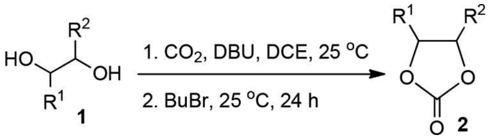
Table 2. Synthesis of 3-etylethylene carbonate from 1,2-butanediol and CO_2.[a]

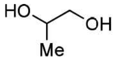
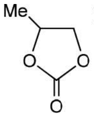
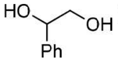
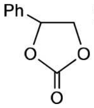
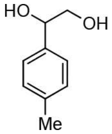
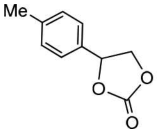
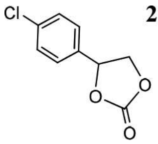
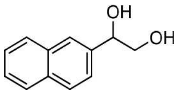
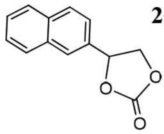
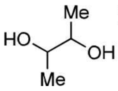
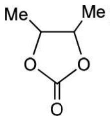
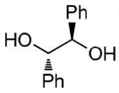
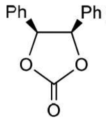
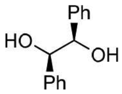
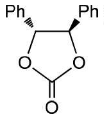
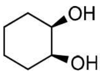
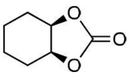
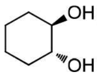
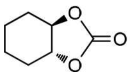


Entry	DBU (mmol)	BuBr (mmol)	Time (h)	Yield (%)[b]
1	10	12	24	63
2	10	12	48	62
3	10	24	24	67
4	15	24	24	71
5	20	24	24	96

[a] Conditions: **1** (2.5 mmol) and 1-bromobutane in DCE (1 mL) at 25 °C.
[b] Yield was determined by ^1H NMR.

Table 3. Synthesis of cyclic carbonates **2** from 1,2-alkanediol **1** and CO_2.[a]



Entry	1,2-Alkanediol	Product	Yield (%)[b]
1	 **1c**	 **2c**	90
2	 **1d**	 **2d**	89
3	 **1e**	 **2e**	84
4	 **1f**	 **2f**	81
5	 **1g**	 **2g**	88
6	 **1h**	 **2h**	95[c]
7	 **1i**	 **2i**	63
8	 **1j**	 **2j**	93
9	 **1k**	 **2k**	60
10	 **1l**	 **2l**	0[d]

[a] Conditions: **1** (2.5 mmol), DBU (20 mmol), and 1-bromobutane (24 mmol) in DCE (1 mL) at 25 °C for 24 h.

[b] Yield was determined by ^1H NMR.

[c] A mixture of stereoisomers.

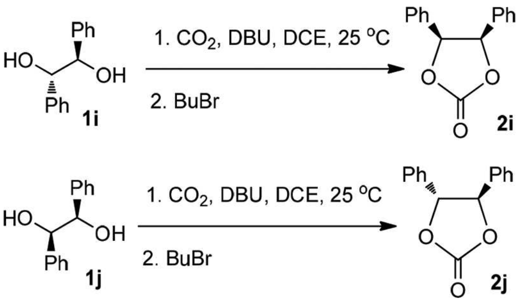
[d] Cyclic carbonates were not formed, but *trans*-1,2-cyclohexanediyl bis(dibutylcarbonate) (**4**) was obtained in 53% yield.

synthesis from CO_2 efficiently takes place in the case of monosubstituted 1,2-ethanediols. Next, we examined the transformation of disubstituted 1,2-ethanediols to cyclic carbonates. When 2,3-butanediol (**1h**) was reacted with CO_2 in the presence of DBU and then treated with 1-bromobutane, 3,4-dimethylethylene carbonate (**2h**) was obtained in 95% yield (entry 6). Because 2,3-butanediol was a mixture of *erythro* and *threo* isomers, the product was also a mixture of *cis* and *trans* isomers. To learn the outcome of the stereochemistry, we conducted the reaction of *threo*-1,2-diphenylethylene glycol (**1i**). When **1i** was reacted with CO_2 in the presence of DBU and followed by treatment with 1-bromobutane, *cis*-3,4-diphenylethylene carbonate (**2i**) was obtained in 63% yield (entry 7). The slightly decreased yield of the product may be attributable to the steric congestion between two phenyl groups in the product, but the reaction provides a pure *cis* isomer. The similar reaction of *erythro*-1,2-diphenylethylene glycol (**1j**) selectively gave *trans*-3,4-diphenylethylene carbonate (**2j**) in 93% yield (entry 8). These results suggest that the present carbonate reaction proceeds stereospecifically, as shown in Scheme 2.

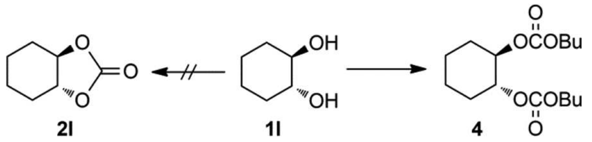
However, a cyclic 1,2-diol shows a different behavior from acyclic diols. *cis*-Cyclohexane-1,2-diol (**1k**) gave cyclic carbonate **2k** in 60% yield, while *trans*-cyclohexane-1,2-diol (**1 l**) did not yield the corresponding cyclic carbonate **2 l** but a double carbonated product **4** was obtained in 53% yield (entries 9 and 10). In the case of *trans*-isomer **1 l**, carbonation takes place readily at each OH groups before cyclization because the intramolecular cyclization may be difficult due to the inherent steric repulsion (Scheme 3).

Although less volatile alkyl halides were suitable for the present reaction due to slow evaporation, a few additional experiments of **1a–c** using iodomethane were examined to determine the effect of alkyl halides on the cyclic carbonate formation. The results are shown in Scheme 4, suggesting that even iodomethane is effective in this reaction.

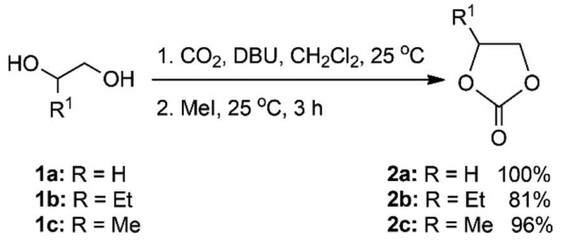
A possible mechanism for the formation of cyclic carbonates **2** from 1,2-diols **1** and CO_2 is proposed in Scheme 5. One OH group of the 1,2-diol undergoes deprotonation by DBU to react with CO_2, giving a carbonate ion.[6] This carbonate ion reacts with 1-bromobutane to form a butylcarbonate. Then, another OH group is deprotonated by DBU to form an alkoxide ion, which undergoes intramolecular nucleophilic addition to the carbonyl carbon to give an ethylene carbonate. Because this intramolecular cyclization is a favorable 5-exo-trig mode,[7] it is considered that the intramolecular process proceeds more efficiently than the intermolecular substitution with 1-bromobutane. The liberated butoxide anion reacts with CO_2 to give dibutyl carbonate after the reaction with 1-bromobutane.



Scheme 2. Stereospecific synthesis of cyclic carbonates.



Scheme 3. Reaction of *trans*-1,2-cyclohexanediol (1 l) with CO_2.



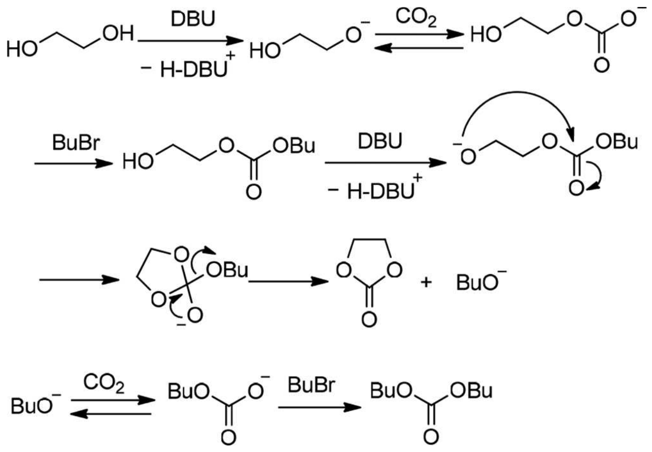
Scheme 4. Reaction of 1,2-diols **1a–c** with CO_2 using iodomethane.

In conclusion, we have demonstrated that several cyclic carbonates can be prepared in good yields directly from CO_2 and 1,2-diols. This cyclic carbonate synthesis is promoted by DBU. This synthesis can be conducted under atmospheric pressure of CO_2 and with one-pot operation. Therefore, this method is very convenient and efficient. It is promising to be applied to synthesis of various useful compounds in the future.

Experimental

Typical procedure for synthesis of 2a from 1a and CO_2

Compound **1a** (5 mmol), DBU (10 mmol), and CH_2Cl_2 (2 mL) were placed in a 50-mL two-necked flask and CO_2 gas was flowed with stirring at 25 °C until the solution was changed to a white suspension. After addition of 1-bromobutane (12 mmol), the flask was capped



Scheme 5. Possible mechanism for ethylene carbonate formation.

with a rubber septum and equipped with a CO_2 balloon. The mixture was stirred at 25 °C for 24 h and then passed through a short pad of silica gel with CH_2Cl_2 as eluent to remove the DBU salts. The eluent was concentrated under reduced pressure and subjected column chromatography on silica gel. Elution with a mixed solvent of CH_2Cl_2 and hexane (3:7) gave dibutyl carbonate (**3**). Elution with CH_2Cl_2 gave **2a**. The yield of the products was determined by ^1H NMR using an internal standard.

General procedure for the synthesis of cyclic carbonates 2

Compound **1** (2.5 mmol) and DBU (20 mmol) in DCE (1 mL) were placed in a 50-mL two-necked flask and CO_2 gas was flowed with stirring at 25 °C until the solution was changed to a white suspension. After addition of 1-bromobutane (24 mmol), the flask was capped with a rubber septum and equipped with a CO_2 balloon. The mixture was stirred at 25 °C for 24 h and then passed through a short pad of silica gel with CH_2Cl_2 as eluent to remove the DBU salts. The eluent was concentrated under reduced pressure and the yield of the product was determined by ^1H NMR using an internal standard. The product **2** was separated by column chromatography on silica gel using hexane and/or CH_2Cl_2 as eluent.

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