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PAPER

Economical synthesis of cyclic carbonates from carbon dioxide and halohydrins using K_2CO_3

Takuji Hirose,[a]* Shinsuke Shimizu,[a] Shujie Qu,[a] Hiroaki Shitara,[a] Koichi Kodama[a] and Lin Wang[a]

A highly simple, economical, and selective synthesis of five-membered cyclic carbonates was achieved by the reaction of CO_2 with 1,2-halohydrins in the presence of K_2CO_3. This method allows the efficient preparation of cyclic carbonates (72–95% yields for monosubstituted cyclic carbonates and 43% for 1,1- and 1,2-disubstituted cyclic carbonates) under mild reaction conditions, atmospheric pressure of CO_2 at 30 °C, and not only in dry DMF, but also in commercial "anhydrous" DMF. The reaction mechanism was elucidated using the SEM and XRD data of the by-products, $KHCO_3$, and KBr.

Introduction

Currently, CO_2 has attracted much attention not only as a major greenhouse gas, but also as an easily available, nontoxic, and abundant C1 resource.[1] From the perspective of global sustainability and environmental concern, the chemical fixation of CO_2 into useful organic compounds is important and has been widely investigated recently. Among them, linear and cyclic carbonates are the most popular targets as they can be used as polar aprotic solvents, electrolytes, fuel additives,[2,3] and intermediates for fine chemicals and polymers.[3,4] Many studies have reported several catalytic systems using metal salts and complexes such as alkali metal halides,[5] metalloporphyrins,[6] and metallosalens[7] and various onium salts as the co-catalyst such as pyridinium,[8] imidazolium,[9] ammonium,[10] and phosphonium salts.[11] *N*-heterocyclic carbenes[12] and functionalized polymeric materials[13] have also been reported to be effective.

For the synthesis of cyclic carbonates, the reaction of CO_2 with an epoxide is the most successful and attractive route as all the atoms of the starting materials are incorporated into the product. We also reported a convenient metal-free system for the cycloaddition of CO_2 to an epoxide using benzyl halide and DMF.[14a] Recently, we succeeded to lower the reaction temperature from 120 °C to 65 °C using a combination of benzyl bromide and DBU.[14b] Moreover, a further advanced organocatalytic system of 2-hydroxymethylpyridine–tetrabutylammonium iodide was developed to lower the reaction temperature; this system is more useful for chiral epoxides.[14c]

Apart from epoxides, 1,2-halohydrins are another class of starting materials for cyclic carbonates. They can be easily prepared by the treatment of alkenes with halogens in the presence of water; they also serve as the starting materials for epoxides. However, only a few methods have been developed for their utility:[15–20] many of them require a high temperature and/or high pressure. Wu *et al.* first reported the synthesis of carbonates from 1,2-halohydrins and CO_2 (20 atm) using K_2CO_3 at 40 °C and reported excellent results.[18] To develop simple and mild reaction procedures,[14] it is necessary to investigate the conversion of CO_2 to cyclic carbonates using 1,2-halohydrins under atmospheric pressure. In this study, we report an economical and effective reaction system to prepare five-membered cyclic carbonates from CO_2 and 1,2-halohydrins in the presence of K_2CO_3 in non-anhydrous and non-deoxygenated DMF.
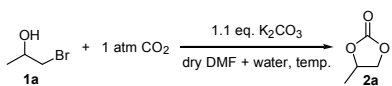
Results and discussion

Based on our previous organocatalytic system,[14a] the effects of several parameters were systematically investigated using excess amount of K_2CO_3 (1.1 mol equiv) as the base in DMF. The reaction of CO_2 with 1-bromo-2-propanol **1a** (containing 22% of 2-bromo-1-propanol) was selected as the model reaction. The effect of the concentration of reaction mixture was studied at 120 °C, and the results are summarized in Table 1 (entries 1–4). When the concentration of **1a** was 1 mmol in 1 mL DMF or lower (entries 1 and 2, Table 1), good yields of >70% were obtained. However, as the concentration increased, the yield decreased to 61% (entry 3) and further decreased to 14% when no solvent was used (entry 4). Probably, the efficient interaction between halohydrin and solid base decreased because of the increased viscosity of the reaction mixture.

At a concentration of 1 mmol (halohydrin)/mL (DMF), the effect of reaction temperature was studied in detail. When the

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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Table 1 Effect of concentration, temperature, and water[a]

Entry	Dry DMF (mL)	Water (µL)	T(°C)	Yield[b] (%)
1	10	0	120	72
2	5	0	120	73
3	3	0	120	61
4	0	0	120	14
5	5	0	100	78
6	5	0	80	81
7	5	0	60	76
8	5	0	40	85
9	5	0	30	90
10	5	0	25	86
11	5	10	120	74
12	5	30	120	72
13	5	50	120	81
14	5	50	30	89
15	5[c]	0	30	90
16	2.5[c]	2500	30	85

[a] Reaction conditions: **1a** (5 mmol; 22% is 2-bromo-1-propanol), K_2CO_3 (0.76 g, 5.5 mmol), CO_2 (99.999%, balloon). After DMF, H_2O (when used), and K_2CO_3 were stirred in the presence of CO_2 (1 atm) for 4 h at the reaction temperature, **1a** was added and reacted for 20 h. [b] Isolated yield. [c] anhydrous (non-anhydrous and non-deoxygenated).

temperature was decreased to 100 °C, 5% increase in the yield was observed (entry 2 vs. entry 5). As the temperature was lowered gradually (entries 6–10), the reaction yield increased as reported previously,[20] and 90% yield was achieved at 30 °C (entry 9). Interestingly, this system works efficiently at ambient temperature (entry 10), significantly lower than the previous systems,[16–19] and corresponds to the systems reported by the Venturello group[15] and Reithofer group.[20]

From the practical perspective of the reaction process, the effect of water content was investigated, and the results are also summarized in Table 1. The amount of water can affect both the solubility of base and concentration of CO_2 in the reaction mixture. A small amount of water from 0.2 vol% to 1 vol% did not affect and resulted in almost the same yield (entries 1 and 11–13) at 120 °C. At 30 °C, DMF containing 1 vol% of water did not affect the reaction yield either (entries 9 and 14). As expected, commercial "anhydrous" (but non-anhydrous and non-deoxygenated) DMF resulted in the same yield as dry DMF at 30 °C (entry 15), i.e., commercial DMF can be directly used as the solvent as received without further purification.

Considering that moisture or a small amount of water does not affect the yield, a DMF/H_2O (1:1 v/v) mixture was investigated; a very good yield of 85% was obtained (entry 16). A slightly lower yield may be caused by the solvation of water to the alcoholate of bromopropanol. Although KOH obtained from water and K_2CO_3 can cause side reactions, neither the corresponding epoxide nor glycol was detected in the reaction

mixture as by-products. It is of practical importance that the DMF amount could be reduced by half.

The effect of some other solvents was investigated at 30 °C, and the results are summarized in Table S1. Apparently, toluene is not a suitable solvent for this reaction (6% yield), because K_2CO_3 was slightly soluble in toluene (entry 1). The use of ethanol as a solvent resulted in a higher yield (62%, entry 2) than toluene, but a lower yield than DMF. In addition to the low solubility of the base, the OH group of EtOH may have contributed to the result as follows: The OH group can compete with the substrate, bromopropanol, for the reaction with K_2CO_3, solvate the alcoholate, and hinder the cyclization reaction. Other aprotic polar solvents such as CH_3CN and DMSO worked well as DMF, resulting in a high yield of 88% similar to previous results.[15] As a much polar solvent, water was used (entry 6); however, the yield was only 32% with almost no by-products. This is probably mainly because of the phase separation of the substrate and aqueous phase.

In this system, a K_2CO_3−DMF suspension was typically exposed to CO_2 for 4 h, and then the cyclization was started by adding halohydrin. The effects of exposure time (t_1) and cyclization time (t_2) were investigated; the results are shown in Table 2. When t_1 was prolonged and t_2 was shortened for 2 h, the yield decreased slightly (entry 2). When only t_1 was shortened to 2 h, the yield was the same (90%, entry 3); however, a much shorter t_1 (0.5 h) lowered the yield to 84% (entry 4). Although a short t_2 of 16 h lowered the yield to 83% (entry 5), further shortening (6 h) decreased the yield by half (44%, entry 6). It can be concluded that more than 18 h of cyclization time is effective after at least 2 h exposure of DMF and the base to CO_2 in this system. It is expected that CO_2 dissolves in the reaction solvent, and a part of CO_2 is activated by the reaction with DMF, nucleophilic activation by DMF,[21] during the exposure time. In the following experiments, 4 h for t_1 and 20 h for t_2 were set as the standard optimum reaction time.

The effect of a base was studied using several types of metal carbonates and potassium hydrogen carbonate ($KHCO_3$); the results are also summarized in Table 2. The use of Na_2CO_3 resulted in a lower yield of 77% (entry 7) than K_2CO_3 (entry 1). It is reported that the solubilization rate of a base in DMF is larger for K_2CO_3 than Na_2CO_3;[22] this might affect the yield. Although Cs_2CO_3 is significantly more soluble than K_2CO_3 in DMF, the yield was almost the same (88%, entry 8). On the other hand, $CaCO_3$ (entry 9) did not afford the product, probably because $CaCO_3$ was almost not soluble in DMF.

The same amount (1.1 mol equiv) of $KHCO_3$ resulted in a lower yield (76%, entry 10) than K_2CO_3, but similar to Na_2CO_3. This result is in contrast to that obtained by Venturello and D'Aloisio.[15] They reported that alkali metal hydrogen carbonates almost did not react. Interestingly, a high yield of 82% was obtained using half the amount (0.55 mol equiv) of K_2CO_3 (entry 11), which was higher than 1.1 equiv of $KHCO_3$. This can be attributed to the difference in the basicity of the salts.
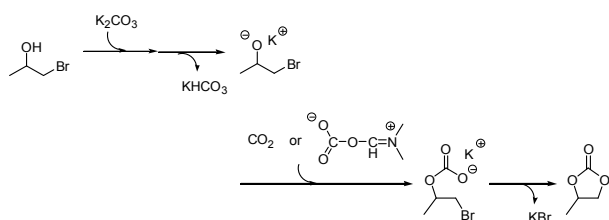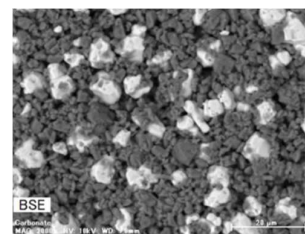
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Table 2 Effects of reaction time and metal carbonate[a]

Entry	Base	Time $(t_1 + t_2)$[b] (h)	Yield[c] (%)
1	K_2CO_3	4 + 20	90
2	K_2CO_3	6 + 18	86
3	K_2CO_3	2 + 20	90
4	K_2CO_3	0.5 + 20	84
5	K_2CO_3	4 + 16	83
6	K_2CO_3	4 + 6	44
7	Na_2CO_3	4 + 20	77
8	Cs_2CO_3	4 + 20	88
9	$CaCO_3$	4 + 20	0
10	$KHCO_3$	4 + 20	76
11	K_2CO_3[d]	4 + 20	82

[a] Reaction conditions: **1a** (5 mmol), base (5.5 mmol), dry DMF (5 mL), CO_2 (99.999%, balloon). [b] After dry DMF and K_2CO_3 were stirred in the presence of CO_2 for t_1 h (exposure time), **1a** was added and reacted for t_2 h (cyclization time) at 30 °C. [c] Isolated yield. [d] 2.75 mmol (0.55 equiv).

As reported previously,[20] the reaction is expected to proceed as shown in Scheme 1: The reaction of halohydrin with K_2CO_3 forms the corresponding potassium alcoholate that reacts with CO_2, which may be activated by DMF as suggested by Kozak et al.[21a] and us.[14a] During the reaction, K_2CO_3 is converted to $KHCO_3$, and KBr is formed after the cyclization. Therefore, the remaining solid in the reaction mixture (the reaction conditions of entry 9 in Table 1) was analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Figure 1 shows the SEM image of the precipitate; clearly, two different types of materials were observed. The energy-dispersive X-ray (EDX) data and XRD profile are shown in Figs. S1 (EDX) and S2 (XRD), respectively. All the data indicated that the precipitate consisted of KBr and $KHCO_3$ without any trace of K_2CO_3.

After these results were obtained, diverse halohydrins were subjected to the optimal reaction conditions, 30 °C in DMF for 24 h (4 h for t_1 and 20 h for t_2), to investigate the substrate scope of this system. As shown in Table 3, the reactions of diverse 1,2-halohydrins with CO_2 solely afforded the corresponding five-membered carbonates regardless of the structure or yield (entries 1–7). Apparently, the use of 1,2-bromohydrins resulted in better yields than 1,2-chlorohydrins (entries 2–4), and the C–Br bond is about 25 times more reactive than the C–Cl bond in **1d** (entry 4). The yield of **2a** (entry 1: 1 atm CO_2, 24 h, 30 °C) is higher than the yield for 2-bromo-2-phenylethanol, 72% (20 atm CO_2, 3 h, 50 °C), in the same solvent, but the conditions were significantly different. For comparison, the reaction was also investigated at 10 atm, and a higher yield of 81% was obtained in 3 h at 30 °C.

Figure 1 SEM image of the precipitate, KBr (white) and $KHCO_3$ (gray), in the reaction mixture (x 2K).

Although the reactions of monosubstituted 1,2-bromohydrins resulted in ~90% yield (entries 1, 4, and 5), a simple bromohydrin, 2-bromoethanol **1b**, resulted in a yield of 81% (entry 2), 10% lower than **1a**. This can be explained by Thorpe–Ingold effect due to the methyl group of **1a**.[23] However, the yields (43%) obtained from the reactions of 1-chloro-2-methyl-2-propanol (**1f**, entry 6) and 2-bromocyclohexanol (**1g**, entry 7) were much lower than the monosubstituted substrates. To improve the yield, the CO_2 pressure was increased to 5 atm, and a better yield of 66% was obtained. However, a further increase to 10 atm was not effective, as the yield obtained was only 67%. The conditions reported by Zhang et al.[20] were not effective as well despite the expected Thorpe–Ingold effect (entry 1, Table 2S). Recent result for **1f** using a new zinc catalyst was also moderate, 50%, at atmospheric pressure of

Table 3 Various cyclic carbonates from halohydrins and CO_2[a]

Entry	Halohydrin	Product	Yield (%)
1	**1a**	**2a**	90 / 81[b]
2	**1b**	**2b**	81
3	**1c**	**2b**	72
4	**1d**	**2d** / **2d'**	**2b**: 88 / **2b'**: 3.5
5	**1e**	**2e**	95
6	**1f**	**2f**	43 / 66[c] / 67[d]
7	**1g**	**2g**	43 / 78[c]
8	**1h**	**2h**	0

[a] Reaction conditions: halohydrin (5 mmol), K_2CO_3 (5.5 mmol), DMF (5 mL), 1 atm CO_2 (99.999%, balloon) at 30 °C for 24 h. [b] 5 atm CO_2, 3 h. [c] 5 atm CO_2, 24 h. [d] 10 atm CO_2, 24 h.

Scheme 1 Proposed mechanism for the coupling reaction of 1-bromo-2-propanol with CO_2 in DMF.

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CO_2 and higher temperature 120 °C.[24] This is, therefore, mainly because of a large steric hindrance to generate monoalkylcarbonate anions, and **1f** is a less reactive chlorohydrin. In contrast, the yield of **2g** further improved to 78% by increasing the CO_2 pressure to 5 atm. Unfortunately, the reaction of a 1,3-halohydrin failed to afford the corresponding cyclic carbonate in this system (entry 8). This result is in contrast with those reported by Zhang et al.[20] They achieved a high yield of six-membered carbonate from 3-chloropropanol using Cs_2CO_3, as confirmed in the present study (Table S2, entry 2). This is probably because of the so-called "cesium effect" for nucleophilic reactions.[25]

Conclusions

In summary, a simple, economical, and selective synthesis of five-membered carbonates was developed from 1,2-halohydrins and CO_2 using K_2CO_3, an inexpensive base, in good-to-high yields under very mild reaction conditions (30 °C, 1 atm CO_2) in DMF. Diverse monosubstituted carbonates were prepared from the corresponding 1,2-halohydrins. This system was also applicable for commercial "anhydrous" DMF, as received without further purification or drying operations. The SEM and XRD analysis of the precipitate showed the formation of $KHCO_3$ and KBr as the by-products, supporting the proposed reaction mechanism for the coupling reaction. Other aprotic polar solvents (CH_3CN, DMSO) and even a DMF/H_2O (1:1 v/v) mixture were shown to be effective in this system. The proposed protocol provides an alternative method for a simple and commercially viable chemical fixation of CO_2 into five-membered cyclic carbonates, not six-membered cyclic carbonates. A difference between K and Cs was observed by comparing previous studies with this study.

Experimental section

All the starting materials and solvents were commercially available. The highest quality products were purchased from Sigma-Aldrich, Wako and Kanto and used as received except dry DMF. Dry DMF was used after fractional distillation from $CaCl_2$ under high vacuum and stored over 4 Å molecular sieves.

The chemical yields refer to the yields of pure isolated substances. All the ^1H and ^{13}C NMR data of the products were consistent with previously reported data except **2f**.[14] (See Supporting Information for the NMR data of **2d**+**2d'** and **2f**). The SEM images were recorded using a Hitachi S-3400N instrument equipped with an EDX analytical system, Bruker XFlash 5010, operated at 10 kV. The XRD patterns were collected using a Bruker D2 Phaser operated at 30 kV and 10 mA equipped with monochromatized $CuK\alpha$ radiation.

General Experimental Procedure

In a 30 mL two-neck flask, K_2CO_3 (5.5 mmol) and DMF (5 mL) were stirred at 30 °C for 4 h under an atmosphere of CO_2 (99.999%, balloon). Then, the halohydrin (5 mmol) was added, and the reaction mixture was stirred for 20 h at the same temperature. After removing the precipitated solid by

filtration, the DMF in the filtrate was removed under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 1:1 v/v (**2a**, **2d**, **2f**) or 2:1 v/v (**2b**, **2e**, **2g**), thus affording the corresponding cyclic carbonate.

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Graphical Abstract

Title: Economical synthesis of cyclic carbonates from carbon dioxide and halohydrins using K_2CO_3

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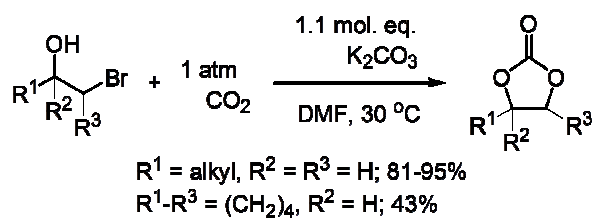
R^1 = alkyl, R^2 = R^3 = H; 81-95%
R^1-R^3 = $(CH_2)_4$, R^2 = H; 43%

Highly simple, economical and selective synthesis of five-membered cyclic carbonates was presented as a reaction of CO_2 and various 1,2-halohydrins using K_2CO_3 at 1 atm of CO_2 and 30 °C in DMF.