



# Effective synthesis of cyclic carbonates from carbon dioxide and epoxides by phosphonium iodides as catalysts in alcoholic solvents



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## ABSTRACT

Phosphonium iodides effectively catalyzed the reaction of CO<sub>2</sub> and epoxides under mild conditions such as ordinary pressure and ambient temperature in 2-propanol, and the corresponding five-membered cyclic carbonates were obtained in high yields.

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## Introduction

The increasing concentration of carbon dioxide (CO<sub>2</sub>) in the atmosphere is partly responsible for the climate changes, while CO<sub>2</sub> is also regarded as a cheap, green C1 resource.<sup>1</sup> CO<sub>2</sub> is an environmentally friendly chemical reagent and is especially useful as a phosgene substitute.<sup>2</sup> One of the most important processes is incorporation of CO<sub>2</sub> into epoxides to give five-membered cyclic carbonates,<sup>3</sup> which are widely used as starting compounds for polycarbonate derivatives,<sup>4</sup> aprotic polar solvents,<sup>5</sup> electrolytes,<sup>6</sup> and lithium ion batteries.<sup>7</sup> Accordingly, a wide range of CO<sub>2</sub> incorporation reactions for the synthesis of cyclic carbonates have been developed, and we have recently reported that the cyclic amidine hydroiodide effectively catalyzed the reaction of CO<sub>2</sub> and epoxides under mild conditions such as ordinary pressure and ambient temperature, and the corresponding five-membered cyclic carbonates were obtained in moderate to high yields.<sup>8</sup> However, the synthesis of functionalized cyclic amidine salts was limited by their strongly basic nature. Additionally, linear<sup>9</sup> and cyclic<sup>10</sup> amidines are, in general, sensitive to moisture. For example, 1,5-diazabicyclo-[3.4.0]non-5-ene (DBN) is quantitatively hydrolyzed by using 2–25 equiv of water at room temperature over 12 h.<sup>10a</sup> On the other hand, phosphonium salts are stable in protic solvents and

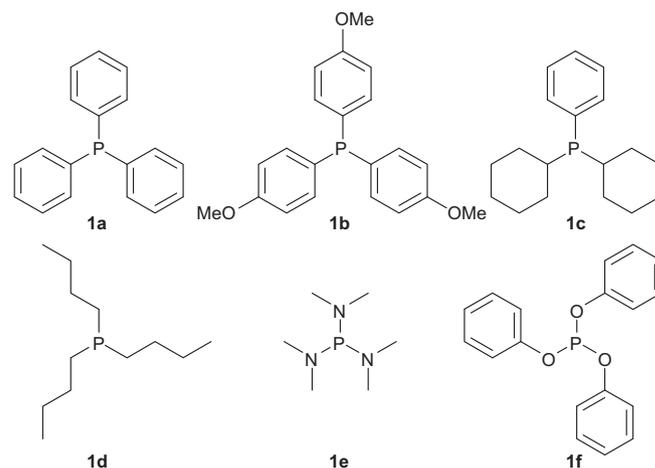


Chart 1. Phosphine derivatives used in this study.

can often be purified by recrystallization from water and/or -alcohol.<sup>11</sup> Phosphonium salts are also used as effective catalysts for the synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>.<sup>12</sup> However, most of these reactions require several tens of atmospheric pressure (20–80 atm) and/or high temperature with the exception of several metal catalyst/phosphonium co-catalyst systems. During the course of our research on the synthesis of cyclic carbonates

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**Scheme 1.** Synthesis of cyclic carbonates from epoxides and  $\text{CO}_2$ .

using various phosphonium salts and solvents, we have found that tertiary and quaternary phosphonium iodides efficiently catalyze the cyclic carbonate-forming reactions from  $\text{CO}_2$  and epoxides in 2-propanol (Chart 1). Herein, we report a novel efficient synthetic method of cyclic carbonates from  $\text{CO}_2$  and epoxides by using a combination of phosphonium iodides and secondary alcohols under mild conditions such as ordinary pressure and ambient temperature (Scheme 1).

## Results and discussion

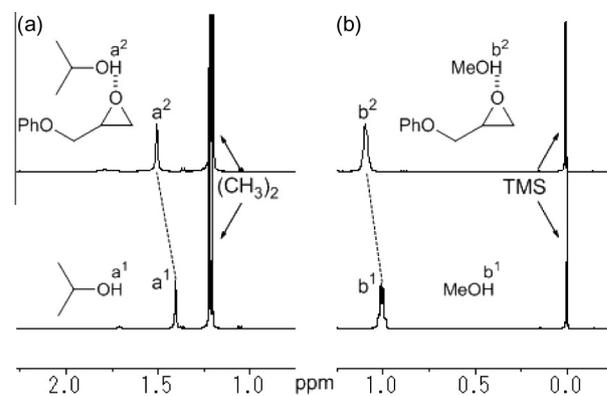
First, we examined the effect of solvent on the carbonate formation from the phenyl glycidyl ether (**2a**) and  $\text{CO}_2$  using the hydroiodide salt (**1a**-HI) at 1 atm and ambient temperature (Table 1). Tetrahydrofuran (THF), an aprotic polar solvent, gave **3a** in a lower yield than that obtained in bulk (entries 1 and 2), although 1,8-diazabicyclo[5.4.0]undec-7-ene hydroiodide (DBU-HI) gave a high yield of **3a** in THF under same conditions.<sup>8</sup> Toluene and chloroform, aprotic non-polar solvents, gave also **3a** in low yields (entries 3 and 4), and the yield of **3a** remarkably decreased in 1-methyl-2-pyrrolidinone (NMP) and dimethyl sulfoxide (DMSO) (entries 5 and 6). These results suggest that neither the aprotic solvents nor **1a**-HI can activate the epoxy ring. On the other hand, protic polar solvents significantly improved the reactivity of **2a** with  $\text{CO}_2$  in the presence of **1a**-HI. Simple primary alcohols such as methanol and ethanol gave **3a** in low yields (entries 7 and 8). In contrast, the use of 2-methylpropyl alcohol resulted in an increased yield of 68%, and the yield was remarkably increased up to 93% when 2-propanol was used as the solvent (entries 9 and 10). Tertiary butyl alcohol gave **3a** in a low yield, which was attributed to the interference of the activation of the epoxy ring in consequence of the bulky *tert*-butyl group (entry 11). The protic solvents can activate the epoxide via hydrogen bonds formed between the

**Table 1**  
Effect of solvent for the synthesis of **2a** by using **1a**-HI under ambient conditions<sup>a</sup>

Entry	Solvent	Yield <sup>b</sup> (%)
1	Bulk	43
2	THF	12
3	Toluene	20
4	$\text{CHCl}_3$	30
5	NMP	2
6	DMSO	Not detected
7	MeOH	4
8	EtOH	26
9	<i>i</i> -BuOH	68
10	<i>i</i> -PrOH	93
11	<i>t</i> -BuOH	57

<sup>a</sup> Reaction conditions: 1 mmol of **2a**, 0.05 mmol of **1a**-HI, 0.2 mL of solvent, 25 °C under 1 atm of  $\text{CO}_2$  for 24 h.

<sup>b</sup> Determined by  $^1\text{H}$  NMR.



**Figure 1.** Partial  $^1\text{H}$  NMR spectra (400 MHz, 25 °C) of a solution of **2a** (110  $\mu\text{mol}$ ) with 2-propanol (55  $\mu\text{mol}$ ) (a) or methanol (55  $\mu\text{mol}$ ) (b) in  $\text{CDCl}_3$  (550  $\mu\text{L}$ ).

hydroxyl and the epoxy groups, which were suggested by the  $^1\text{H}$  NMR spectrum of **2a** with alcohols in  $\text{CDCl}_3$  (Fig. 1). It was found that the OH-proton signal of 2-propanol shifted from 1.41 ppm to a lower magnetic field of 1.50 ppm at ambient temperature despite being diluted with  $\text{CDCl}_3$ . Hydroxyl protons of other alcohols (ethanol, isobutyl alcohol, and *tert*-butanol) shifted similar to 2-propanol. Although the OH-proton signal of methanol also shifted from 1.01 ppm to a lower magnetic field of 1.09 ppm, the product yield in methanol was much lower than that obtained in 2-propanol. This could be accounted for by methanol's stronger ability to solvate the iodide anion than 2-propanol,<sup>13</sup> which hampers the nucleophilic attack of the iodide anion to the epoxy group (this point is discussed later in Table 4).

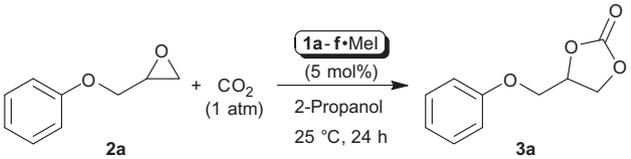
Next, we investigated the effect of the counter anions of **1a** salts on the carbonate formation from **2a** and  $\text{CO}_2$  in 2-propanol at 1 atm and ambient temperature (Table 2). Several phosphonium chlorides catalyze the reaction of epoxides and  $\text{CO}_2$  under relatively severe conditions such as 30 atm and 160 °C or supercritical conditions.<sup>12d</sup> However, neither triphenylphosphine hydrochloride (**1a**-HCl) nor methyltriphenylphosphonium chloride (**1a**-MeCl) gave much cyclic carbonate (**2a**) at 1 atm and 25 °C for 24 h (entries 1 and 2). In contrast, the hydrobromide (**1a**-HBr) and the phosphonium bromide (**1a**-MeBr) resulted in increased yields of 32% and 37%, respectively (entries 3 and 4), when the hydroiodide (**1a**-HI) and the phosphonium iodide (**1a**-MeI) were used as the catalyst, the yield of **3a** was remarkably increased up to 93% and 97%,

**Table 2**  
Effect of anion moiety of catalyst for the synthesis of **2a** under ambient conditions<sup>a</sup>

Entry	Catalyst	Yield <sup>b</sup> (%)
1	<b>1a</b> -HCl	2
2	<b>1a</b> -MeCl	7
3	<b>1a</b> -HBr	32
4	<b>1a</b> -MeBr	37
5	<b>1a</b> -HI	93
6	<b>1a</b> -MeI	97
7	$\text{PPh}_3$	Not detected
8	$\text{P}(\text{O})\text{Ph}_3$	Not detected

<sup>a</sup> Reaction conditions: 1 mmol of **2a**, 0.05 mmol of **1a**-RX, 0.2 mL of 2-propanol, 25 °C under 1 atm of  $\text{CO}_2$  for 24 h.

<sup>b</sup> Determined by  $^1\text{H}$  NMR.

**Table 3**  
Effect of structure of catalyst for the synthesis of **2a** under ambient conditions<sup>a</sup>


Entry	Catalyst	Yield <sup>b</sup> (%)
1	<b>1a</b> -Mel	97
2	<b>1b</b> -Mel	87
3	<b>1c</b> -Mel	84
4	<b>1d</b> -Mel	89
5	<b>1e</b> -Mel	87
6	<b>1f</b> -Mel	Not detected

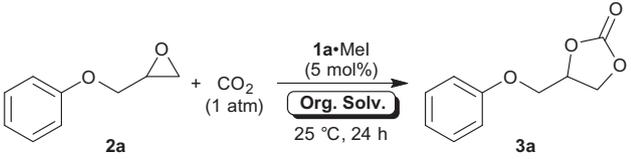
<sup>a</sup> Reaction conditions: 1 mmol of **2a**, 0.05 mmol of **1a–f**-Mel, 0.2 mL of 2-propanol, 25 °C under 1 atm of CO<sub>2</sub> for 24 h.

<sup>b</sup> Determined by <sup>1</sup>H NMR.

respectively (entries 5 and 6). The use of phosphine ligands without counter anion gave no cyclic carbonate (entries 7 and 8). The catalytic activity is thus highly affected by the counter anion of the catalysts.

Furthermore, we examined various phosphonium iodides (**1a–f**-Mel) in the carbonate formation from **2a** and CO<sub>2</sub> in 2-propanol at 1 atm and ambient temperature (Table 3). Catalytic activities of the phosphonium salts bearing substituents more electron-rich than **1a**-Mel (**1b–d**-Mel) were slightly less than that of **1a**-Mel (entries 1–4). The phosphonium iodide with dimethylamino groups resulted in more or less the same yield as **1b–d**-Mel (entry 5). In contrast, the phosphonium iodide with phenoxy substituents (**1f**-Mel) gave no cyclic carbonate (entry 6). Thus, the methyltriphenylphosphonium iodide (**1a**-Mel) was the best catalyst among the phosphonium salts investigated here (**1a–f**-RX).

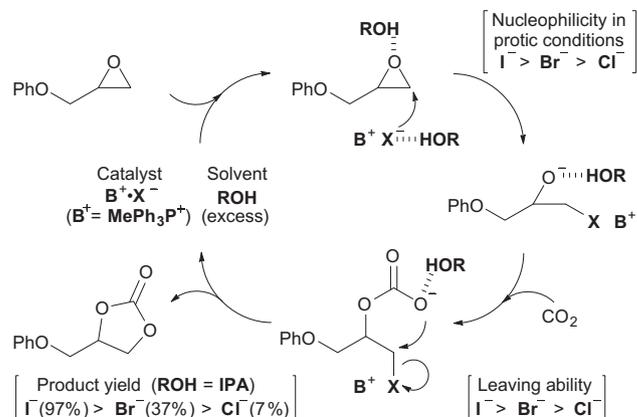
Next, the carbonate formation of **2a** with CO<sub>2</sub> was carried out in several secondary alcohols and other solvents using **1a**-Mel (Table 4). As in the case of **1a**-HI, THF and methanol gave **2a** in low yields (entries 1 and 2), and the yield of **2a** was not obtained in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (entry 3). In contrast, both 1-methoxy-2-propanol and 2-propanol resulted in almost quantitative yields (entries 4 and 5). The reaction efficiency was thus significantly affected by the structures of the secondary alcohols (entries 3–5). These results could be explained in terms of the solvation of the halide anions. The protic solvents activate the epoxide via hydrogen bonds as described above, while they strongly solvate iodide anion, thereby diminishing the reactivity

**Table 4**  
Effect of solvent on the synthesis of **2a** by using **1a**-Mel under ambient conditions<sup>a</sup>


Entry	Solvent	Yield <sup>b</sup> (%)
1	THF	35
2	MeOH	30
3	(CF <sub>3</sub> ) <sub>2</sub> CHOH	Not detected
4	(MeOCH <sub>2</sub> )(CH <sub>3</sub> )CHOH	99
5	(CH <sub>3</sub> ) <sub>2</sub> CHOH	97

<sup>a</sup> Reaction conditions: 1 mmol of **2a**, 0.05 mmol of **1a**-Mel, 0.2 mL of solvent, 25 °C under 1 atm of CO<sub>2</sub> for 24 h.

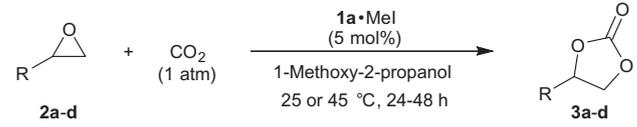
<sup>b</sup> Determined by <sup>1</sup>H NMR.

**Scheme 2.** A plausible mechanism for catalyzed synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>.

of the ring-opening reaction. In fact, the product yields decreased with increasing acceptor number (AN) of solvents, that is, IPA (33.8) < MeOH (41.3) < HFIP (63.0), which are known to be proportional to the solvation ability.<sup>13</sup>

A plausible mechanism for the catalytic synthesis of carbonate is shown in Scheme 2. Initially, the protic solvent activates the epoxide, and at the same time solvates the halide anion of the catalyst through hydrogen bonds. Then, the ring-opening intermediate is formed by the nucleophilic attack of the halide anion on the activated epoxy group, and subsequent nucleophilic attack on CO<sub>2</sub> leads to the alkylcarbonate anion. Finally, the ring-closure through the elimination of the halide anion gives the cyclic carbonate. In the reaction, the protic solvents play two opposite roles, that is, activation of the epoxy ring via hydrogen bonds and diminishing the reactivity of the halide anion through solvation. The latter is the dominant factor for the catalytic activity, which can be roughly indicated by the acceptor numbers. The counter anion of the catalysts is another important factor of the catalytic activity, which was in the order of iodide > bromide > chloride. This could be accounted for by the nucleophilicity of halide anions in protic solvents at the ring-opening step as well as the leaving ability at the ring-closing step, both in the order of  $I^- > Br^- > Cl^-$ .

Finally, we examined the carbonate-forming reactions of other epoxides with **1a**-Mel and 1-methoxy-2-propanol at 25 or 45 °C (Table 5).<sup>14</sup> The carbonate (**3a**) was isolated quantitatively by short

**Table 5**  
Synthesis of various cyclic carbonates by using **1a**-Mel under ambient conditions<sup>a</sup>


a: R = PhOCH<sub>2</sub>, b: R = ClCH<sub>2</sub>, c: R = CH<sub>2</sub>=C(CH<sub>3</sub>)CO<sub>2</sub>CH<sub>2</sub>, d: R = *n*-Bu

Entry	Epoxide	Temp (°C)	Time (h)	Yield <sup>b</sup> (%)
1	<b>2a</b>	25	24	99 (99) <sup>c</sup>
2	<b>2b</b>	25	24	90
3	<b>2b</b>	25	36	98 (97) <sup>c</sup>
4	<b>2c</b>	25	24	96
5	<b>2c</b>	25	36	>99 (>99) <sup>c</sup>
6	<b>2d</b>	25	24	65
7	<b>2d</b>	25	48	86
8	<b>2d</b>	45	24	92 (91) <sup>c</sup>

<sup>a</sup> Reaction conditions: 1 mmol of **2a–d**, 0.05 mmol of **1a**-Mel, 0.2 mL of 1-methoxy-2-propanol, 25 or 45 °C under 1 atm of CO<sub>2</sub> for 24–48 h.

<sup>b</sup> Determined by <sup>1</sup>H NMR.

<sup>c</sup> Isolated yields are in parentheses.

column chromatography on silica gel (entry 1). Epichlorohydrin (**2b**) and glycidyl methacrylate (**2c**) containing electron withdrawing groups on the carbon atom next to the epoxy group that were as reactive as **2a** (entries 2–5), while the epoxide bearing hydrocarbon substituents, 1,2-epoxyhexane (**2d**), had a lower reactivity than those of other epoxides (entries 6 and 7). When the reaction temperature was raised from 25 to 45 °C, the conversion of **2d** increased and the cyclic carbonate (**3d**) was isolated in high yield (entry 8). Other reported reactions using protic compounds for the activation of epoxide require several tens of atmospheric pressure (20–40 atm) and high temperature (80–140 °C).<sup>12e,15</sup>

In conclusion, we have demonstrated that the phosphonium iodides catalyzed effectively the reactions of CO<sub>2</sub> and epoxides in secondary alcohols and the corresponding cyclic carbonates are obtained in reasonable yields under mild conditions such as ordinary pressure and 25–45 °C. The catalytic activity is highly affected by the counter anions of the phosphonium catalysts; the iodides catalyze efficiently the carbonate-forming reactions, in contrast to the bromide and chloride counterparts that show low reactivity. The choice of the solvent is also important. The protic solvents with low acceptor numbers can activate the epoxy group without diminishing the nucleophilicity of the halide anions through strong solvation.

#### Supplementary data

Supplementary data (<sup>1</sup>H and <sup>13</sup>C spectra of isolated compounds and experimental data of phosphonium halides) associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2013.10.068>.

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- General procedure for five-membered cyclic carbonate (2a–d)*: Methyltriphenylphosphonium iodide (20.2 mg, 0.05 mmol) was added to a solution of epoxide (1 mmol) in 1-methoxy-2-propanol (0.2 mL). The atmosphere inside the flask was replaced with CO<sub>2</sub> (balloon, ca. 1 atm), and the reaction mixture was stirred at 25 or 45 °C. After 24–48 h, the mixture was cooled to rt, and evaporated in vacuo. The residue was purified by silica gel column chromatography (eluent: CHCl<sub>3</sub>) to give the corresponding cyclic carbonate (91–99%).
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