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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_2 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.

Introduction

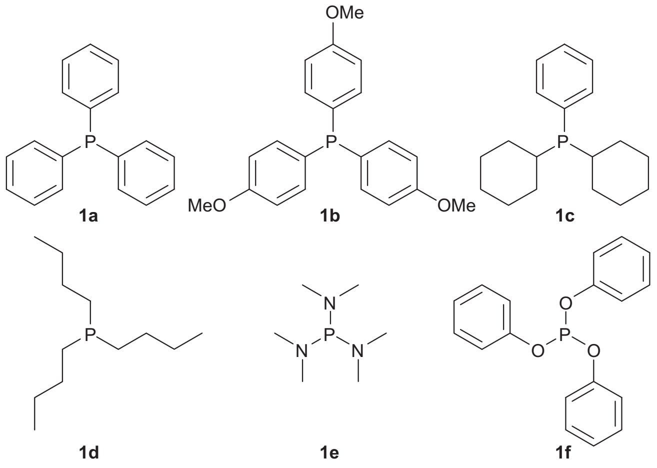

Chart 1. Phosphine derivatives used in this study.

The increasing concentration of carbon dioxide (CO_2) in the atmosphere is partly responsible for the climate changes, while CO_2 is also regarded as a cheap, green C1 resource.[1] CO_2 is an environmentally friendly chemical reagent and is especially useful as a phosgene substitute.[2] One of the most important processes is incorporation of CO_2 into epoxides to give five-membered cyclic carbonates,[3] which are widely used as starting compounds for polycarbonate derivatives,[4] aprotic polar solvents,[5] electrolytes,[6] and lithium ion batteries.[7] Accordingly, a wide range of CO_2 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_2 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.[8] However, the synthesis of functionalized cyclic amidine salts was limited by their strongly basic nature. Additionally, linear[9] and cyclic[10] 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.[10a] On the other hand, phosphonium salts are stable in protic solvents and can often be purified by recrystallization from water and/or -alcohol.[11] Phosphonium salts are also used as effective catalysts for the synthesis of cyclic carbonates from epoxides and CO_2.[12] 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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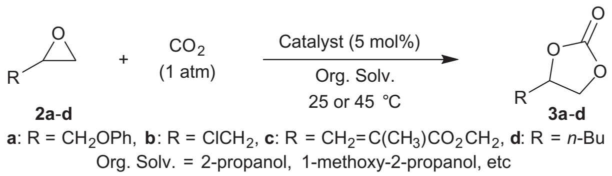


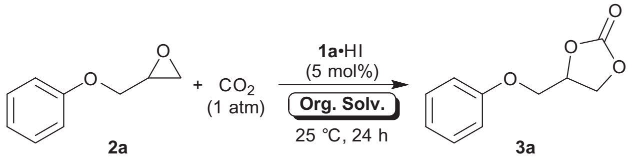
Scheme 1. Synthesis of cyclic carbonates from epoxides and CO_2.

using various phosphonium salts and solvents, we have found that tertiary and quaternary phosphonium iodides efficiently catalyze the cyclic carbonate-forming reactions from CO_2 and epoxides in 2-propanol (Chart 1). Herein, we report a novel efficient synthetic method of cyclic carbonates from 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 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.[8] 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 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 hydroxyl and the epoxy groups, which were suggested by the ^1H NMR spectrum of **2a** with alcohols in $CDCl_3$ (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 $CDCl_3$. 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,[13] which hampers the nucleophilic attack of the iodide anion to the epoxy group (this point is discussed later in Table 4).

Table 1
Effect of solvent for the synthesis of **2a** by using **1a**·HI under ambient conditions[a]



Entry	Solvent	Yield[b] (%)
1	Bulk	43
2	THF	12
3	Toluene	20
4	$CHCl_3$	30
5	NMP	2
6	DMSO	Not detected
7	MeOH	4
8	EtOH	26
9	*i*-BuOH	68
10	*i*-PrOH	93
11	*t*-BuOH	57

[a] Reaction conditions: 1 mmol of **2a**, 0.05 mmol of **1a**·HI, 0.2 mL of solvent, 25 °C under 1 atm of CO_2 for 24 h.
[b] Determined by ^1H NMR.

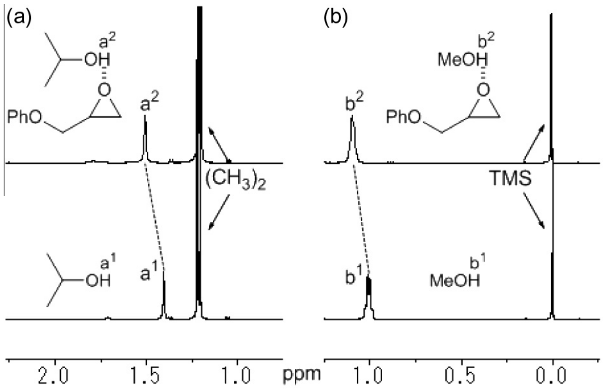
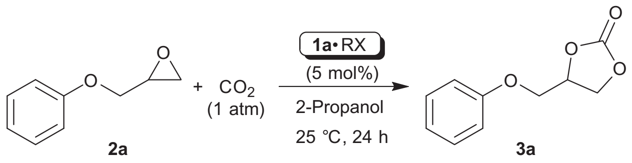


Figure 1. Partial ^1H NMR spectra (400 MHz, 25 °C) of a solution of **2a** (110 µmol) with 2-propanol (55 µmol) (a) or methanol (55 µmol) (b) in $CDCl_3$ (550 µL).

Next, we investigated the effect of the counter anions of **1a** salts on the carbonate formation from **2a** and CO_2 in 2-propanol at 1 atm and ambient temperature (Table 2). Several phosphonium chlorides catalyze the reaction of epoxides and CO_2 under relatively severe conditions such as 30 atm and 160 °C or supercritical conditions.[12d] 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[a]



Entry	Catalyst	Yield[b] (%)
1	**1a**·HCl	2
2	**1a**·MeCl	7
3	**1a**·HBr	32
4	**1a**·MeBr	37
5	**1a**·HI	93
6	**1a**·MeI	97
7	PPh_3	Not detected
8	$P(O)Ph_3$	Not detected

[a] Reaction conditions: 1 mmol of **2a**, 0.05 mmol of **1a**·RX, 0.2 mL of 2-propanol, 25 °C under 1 atm of CO_2 for 24 h.
[b] Determined by ^1H NMR.