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Letter

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Tetraarylphosphonium Salt-Catalyzed Carbon Dioxide Fixation at Atmospheric Pressure for the Synthesis of Cyclic Carbonates

Yasunori Toda,* Yutaka Komiyama, Ayaka Kikuchi, and Hiroyuki Suga*

Department of Materials Chemistry, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380-8553, Japan

ABSTRACT: Phosphonium salts exhibit many of utilities in organic synthesis. However, tetraarylphosphonium salts (TAPS) have found limited use as catalysts. We demonstrate the TAPS-catalyzed carbon dioxide fixation at atmospheric pressure for the coupling reaction with epoxides. 5-Membered cyclic carbonates were obtained, including enantio-enriched carbonates. Mechanistic studies revealed the origin of the behavior of TAPS to be the *in situ* formation of an active species by TAPS addition to epoxides *via* halohydrin intermediates.

KEYWORDS: chemical fixation, carbon dioxide, epoxides, cyclic carbonates, phosphonium salts

Phosphonium salts are phosphorus(V) compounds featuring a tetrahedral phosphonium cation, and are widely used in organic synthesis as precursors of Wittig reagents, phase transfer catalysts, ionic liquids, and other applications.[1] Tetraarylphosphonium salts (TAPS) with the formula $[Ar^1(Ar^2)_3P^+]X^-$ can be readily prepared by coupling reactions of an aryl halide (Ar^1-X) and a triarylphosphine ($(Ar^2)_3P$), which are stereoelectronically tunable.[2] The exploration of TAPS function especially for catalysis is hence attractive, but their catalytic ability has remained unexploited.[1n] It is expected that TAPS **1** might serve as a bifunctional catalyst composed of a Brønsted acidic site and a nucleophilic site by introduction of a hydroxyl group on an aromatic ring (Figure 1). We reasoned that chemical fixation of carbon dioxide (CO_2) with epoxides **2** to produce cyclic carbonates **3** would be a suitable target for validating this catalyst design because Brønsted acid-activation of an epoxide **2** by a TAPS **1** could facilitate the epoxide ring-opening step by the counter anion (X^-) of a TAPS.[3,4] This devised system raised the inherent question of not only whether the activation of epoxides was possible but also whether the carbonate product by incorporation of CO_2 could be obtained. In fact, to the best of our knowledge, there are no examples of TAPS-catalyzed CO_2 fixation reactions, and the challenge inspired us to probe a novel application of TAPS as interesting catalysts.

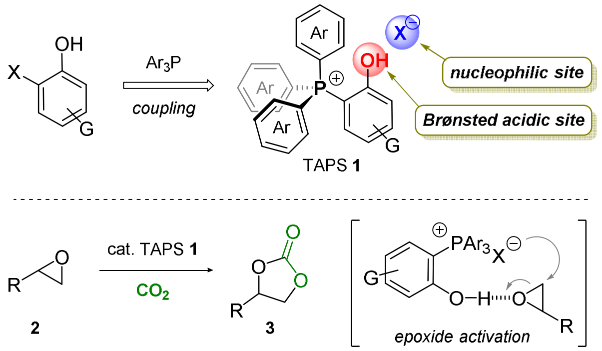


Figure 1. Working hypothesis: The design of TAPS as a bifunctional catalyst for the coupling of CO_2 and epoxides.

CO_2 holds great potential as an abundant, inexpensive, nonflammable, nontoxic, and renewable C1 building block.[5] The chemical fixation of CO_2 into valuable products has recently received much attention. One of the most well-known methods is the coupling of CO_2 and epoxides for the synthesis of 5-membered cyclic carbonates.[6] Considerable effort has been devoted to the development of efficient catalytic systems for this transformation, especially Lewis acidic metal-based systems.[7,8] The use of bifunctional catalysts consisting of an electrophilic metal ion and a nucleophilic halide ion significantly accelerates the process under mild conditions.[8f,g] Meanwhile, the area of organocatalysis for the CO_2 coupling with epoxides is relatively limited,[9] despite the fact that bifunctional strategies are particularly utilized in organocatalytic reactions[10] In addition, it is still challenging to perform the reaction at ambient CO_2 pressure. Although quaternary ammonium and phosphonium salts are commonly employed for the CO_2 fixation,[11] in contrast to metal catalysis, bifunctional catalysts based on onium salts have been rarely reported.[4] We posited that a hydrogen bond donor, a hydroxyl group properly attached to a TAPS, might promote the CO_2 insertion into epoxides through synergistic effects of an ionic Brønsted acid and a halide ion. Here, we demonstrate the first use of TAPS **1** for the chemical fixation of CO_2 with epoxides **2** at *atmospheric* pressure, leading to cyclic carbonates **3**. Moreover, the present study emphasizes the importance of functional and structural requirements of TAPS for the activation of epoxides.

At the outset of our study, we prepared TAPS **1a** from 2-bromo-*p*-cresol in only one-step by using Pd-catalyzed coupling reaction with triphenyl phosphine, and attempted X-ray crystallographic analysis (Figure 2). In the crystalline state, **1a** exists as a hydrate form, and hydrogen bonding between the hydroxyl group of **1a** and the water molecule was inferred based on the distance of the two oxygen atoms: O(1)H−O(2) = 2.581 Å. This implies that ionic Brønsted acid **1** could activate an epoxide through hydrogen bond interaction, and motivated us to investigate the CO_2 fixation.

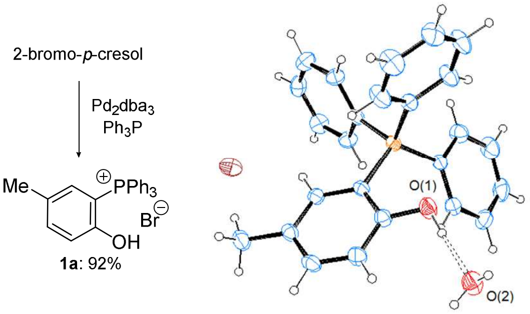


Figure 2. Preparation and ORTEP drawing (30% probability ellipsoids) of TAPS **1a**.

The initial experiment was performed using styrene oxide (**2a**), 10 mol% of TAPS **1a**, and a balloon of CO_2 in *o*-xylene at 120 °C for 12 hours (Table 1, entry 1). The reaction afforded desired product **3a** in low, but promising yield (41%). Different types of catalysts **4**-**8** including ammonium salt **7** were then screened, because TAPS **1** could potentially catalyze the ring-opening step in an intermolecular manner (Table 1, entries 2-6). Interestingly, none of the catalysts yielded the product, and starting material **2a** was nearly completely recovered. These results clearly showed that the *ortho*-hydroxyl group of **1a** and phosphonium moiety were crucial in the reaction progress, implying the importance of bifunctional catalysis. This was supported by an experiment employing catalytic amounts (10 mol%) of phenol and tetraphenylphosphonium bromide (**8**) to see conversion of **2a** (Table 1, entry 7). As expected, only a trace amount of **3a** was obtained, and phenol itself did not yield **3a** (Table 1, entry 8). Other Brønsted acid/nucleophilic Lewis base binary systems were also investigated, but were not effective compared with **1a** (Table 1, entries 9 and 10). Switching the solvent to chlorobenzene and increasing the concentration improved the yield up to 78%, and finally, the use of 15 mol% of **1a** afforded **3a** in 90% isolated yield (Table 1, entries 11-13).[12] Next, the electronic effect of the substituents on the phenol moiety was investigated to learn if the Brønsted acidity of the hydroxyl group in **1** would affect the reaction progress (Table 1, entries 14 and 15). To our surprise, introduction of a strong electron-withdrawing group (**1b**: G = CF_3) resulted in low yield, whereas an electron-donating group (**1c**: G = OMe) did not change the activity. It should be noted that the use of **1b** afforded a bromohydrin intermediate in 11% yield by ^1H NMR. In addition, we scrutinized the effects of counter anions of TAPS **1** (Table 1, entries 16-18). TAPS **1d**, having an iodide ion (I^-), marginally decreased the yield, even though the nucleophilicity of I^- is stronger than Br^- in aprotic solvent (Table 1, entry 16). On the other hand, the attempts using TAPS **1e** and **1f**, involving less-nucleophilic counter anions such as triflate (TfO^-) and hexafluorophosphate (PF_6^-), led to no formation of cyclic carbonate **2a** (Table 1, entries 17 and 18). It is obviously shown that a nucleophilic counter anion is necessary to obtain the cyclic carbonates.

The initial scope of substrates **2** is summarized in Table 2. Styrene oxide derivatives **2b** and **2c** afforded the products in good yields, and terminal epoxides **2d-g**, bearing halide, amino, and alkyl groups also underwent the CO_2 fixation effectively. Moreover, glycidol derivatives **2h-n** were examined, and various substituents on the ether oxygen atom were tolerated to give the products in moderate to high yields.

Table 1. Screening of catalysts and optimization of the reaction conditions[a]

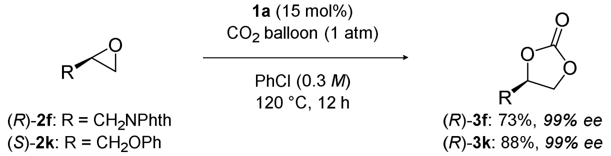
Entry	catalyst (mol%)	solvent (*M*)	yield[b] (%)
1	**1a**: G = Me, X = Br	*o*-xylene (0.1)	41
2	**4** (10)	*o*-xylene (0.1)	<2
3	**5** (10)	*o*-xylene (0.1)	<2
4	**6** (10)	*o*-xylene (0.1)	<2
5	**7** (10)	*o*-xylene (0.1)	<2
6	**8**: Ph_4PBr (10)	*o*-xylene (0.1)	<2
7	PhOH (10) + **8** (10)	*o*-xylene (0.1)	<2
8	PhOH (10)	*o*-xylene (0.1)	<2
9	PhOH (10) + DMAP (10)	*o*-xylene (0.1)	<2
10	TsOH (10) + Py [PPTS] (10)	*o*-xylene (0.1)	<2[c,d]
11	**1a** (10)	PhCl (0.1)	54
12	**1a** (10)	PhCl (0.3)	78
13	**1a** (15)	PhCl (0.3)	90 (90)
14	**1b**: G = CF_3, X = Br (15)	PhCl (0.3)	35
15	**1c**: G = OMe, X = Br (15)	PhCl (0.3)	86
16	**1d**: G = Me, X = I (15)	PhCl (0.3)	85
17	**1e**: G = Me, X = OTf (15)	PhCl (0.3)	<2[d]
18	**1f**: G = Me, X = PF_6 (15)	PhCl (0.3)	<2[d]

[a] Unless otherwise noted, all reactions were carried out on a 0.20 mmol scale using styrene oxide (**2a**) under a balloon of CO_2 at 120 °C for 12 h. See Supporting Information for details. [b] Determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard (Isolated yield is shown in parentheses). [c] Full conversion of **2a**. [d] Phenylacetaldehyde was observed as a major by-product.

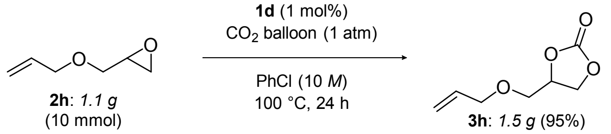
Table 2. Substrate scope of TAPS-catalyzed CO_2 fixation at atmospheric pressure[a]

[a] Unless otherwise noted, all reactions were carried out on a 0.30 mmol scale using epoxides **2** under a balloon of CO_2 in PhCl at 120 °C for 12 h. See supporting Information for details.

Taking into account the system established, enantio-pure epoxides were submitted to the optimized reaction conditions to give the optically active carbonates (Scheme 1). In spite of the utility of 5-membered cyclic carbonates in asymmetric synthesis,[13] only a few examples have been described where they were obtained in nearly enantio-pure form by hydrogen bond donor-catalyzed CO_2 fixation reactions.[3j,10e] To our delight, enantiomerically pure and commercially available epoxides (*R*)-**2f** and (*S*)-**2k** were converted to the corresponding cyclic carbonates with high enantiomeric excesses, respectively (**3f**: 99% ee, **3k**: 99% ee). These results suggested that regioselective ring-opening proceeds at the methylene C−O bond of terminal epoxides (β attack) because ring-opening at the methine C−O bond (α attack) would cause racemization of the chiral center. Furthermore, the reaction was performed on gram-scale by using 1 mol% of TAPS **1d**, affording **3h** in excellent yield (Scheme 2). Compared with other reported hydrogen bond catalysis,[3,4] the loading of TAPS is privileged while somewhat high temperature is needed. For this scale-up process, the use of **1d**, bearing I^- as a counter anion, with a higher concentration of solvent drastically accelerated the CO_2 fixation (See Supporting Information).

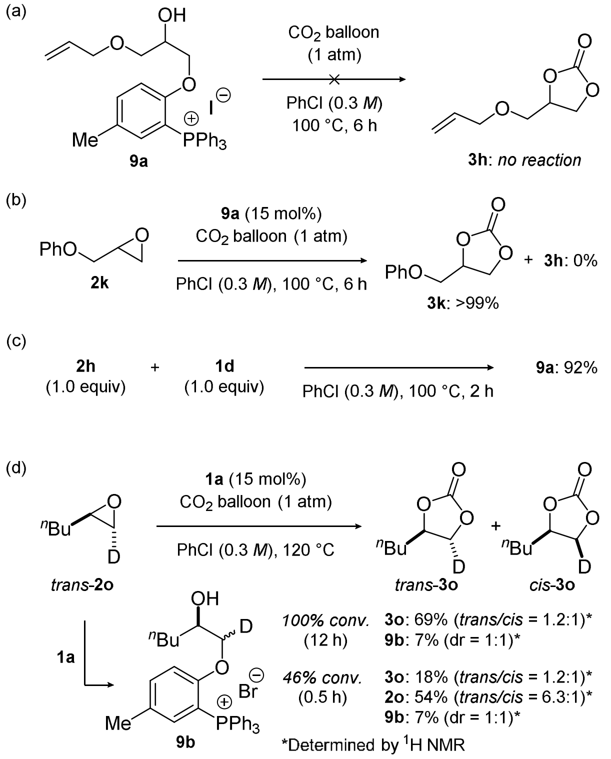


Scheme 1. Optically active carbonate synthesis



Scheme 2. Gram-scale synthesis

In pursuit of practical application, we tried to recycle TAPS after the reaction. Unexpectedly, the epoxide adduct **9a** was recovered instead of **1d** by silica gel column chromatography. To identify whether **9a** was a dead-end product of the catalytic cycle or not, control experiments shown in Scheme 3 were conducted. a) First, **9a** was submitted to the CO_2 fixation conditions, however, no carbonate **3h** was obtained at all. b) By contrast, the treatment of 15 mol% of **9a** with epoxide **2k** cleanly afforded the corresponding carbonate **3k** as the sole product, and **9a** was not changed at the end of the transformation (~95% recovery of **9a** by ^{1}H NMR).[14] c) The stoichiometric reaction using **1d** in the absence of CO_2 was also examined, leading to the formation of the adduct **9a** (92%). These results strongly suggested TAPS **1d** was added to epoxide **2h** *in situ* to generate **9a** that catalyzed the overall process. Next, we investigated the reaction of *trans*-deuterated epoxide **2o** to gain mechanistic insight into the initial epoxide ring-opening step (Scheme 3d).[3a,8g,9b] Curiously, *trans*-**2o** was transformed to the mixture of *trans*- and *cis*-**3o** (69%), and the adduct **9b** (7%). It should be emphasized that stereochemistry information at the β-carbon of *trans*-**2o** was significantly lost under the reaction conditions. Thus, we postulated that the ring-opening of epoxides would proceed with the help of halide ions and be reversible, allowing for scrambling of the β-carbon stereocenter presumably due to a halide ion exchange on alkyl halides.[3b] Indeed, *cis*-**2o** was observed during the course of the reaction, which is consistent with our mechanistic assumption. Based on the above studies, we concluded that the formation of **9** from **2** could involve halohydrin intermediates initiated by bifunctional epoxide activation of **1**.[15] Notably, the experimental results also imply that the rate-determining step of the whole transformation might be attributed to CO_2 capture because of the evidence that epoxide **2o** epimerized rapidly.



Scheme 3. Mechanistic studies

In summary, we have demonstrated the utility of TAPS **1** for CO_2 transformation to cyclic carbonates under atmospheric pressure. Various terminal epoxides were converted into corresponding 5-membered cyclic carbonates with good to excellent yields, including highly enantio-enriched carbonates. The origin of the unique behavior of **1** has been identified by mechanistic studies, and the results suggested that the epoxide adduct of TAPS would be an active species for the CO_2 fixation. As often encountered, serendipity as well as rational design of catalyst played an important role in the catalysis development. Efforts to cultivate functions of TAPS as fascinating catalysts will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures (PDF), spectroscopic data for all new compounds (PDF), and crystallographic data for **1a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: ytoda@shinshu-u.ac.jp (Y.T.)
*E-mail: sugahio@shinshu-u.ac.jp (H.S.)

Notes

The authors declare no competing financial interest.

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(12) No conversion of **2a** was observed in the absence of TAPS **1a** under the same reaction conditions. Detailed optimization of reaction conditions is shown in Supporting Information.

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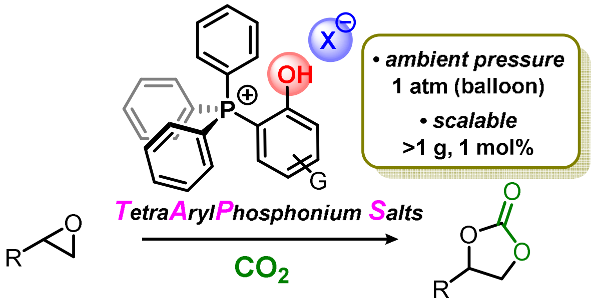
(14) **2h** was quantitatively converted to **3h** under the same conditions in Scheme 3b.

(15) If the phenolic oxygen of TAPS **1** attacks not halohydrins but epoxides, the formation of **9** from **2** would not be reversible. This was supported by the experiments in Scheme 3a and 3b.


X
OH
P
G
• *ambient pressure*
1 atm (balloon)
• *scalable*
>1 g, 1 mol%
TetraArylPhosphonium Salts
CO2
R
O
R
O
O
O