HETEROCYCLES, Vol. 103, No. 1, 2021, pp. 94 - 109. © 2021 The Japan Institute of Heterocyclic Chemistry
Received, 25th May, 2020, Accepted, 1st July, 2020, Published online, 17th July, 2020
DOI: 10.3987/REV-20-SR(K)2

ENVIRONMENTALLY BENIGN SYNTHESIS OF CYCLIC CARBONATES FROM EPOXIDES AND CARBON DIOXIDE USING BINARY AND BIFUNCTIONAL CATALYSTS

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Dedicated to Professor Yasuyuki Kita on the occasion of his 77th birthday

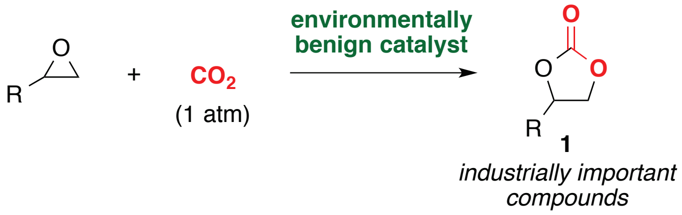
Abstract – The extensive utility of five-membered cyclic carbonates has been well established in the chemical industry. Among the various methods available for the synthesis of five-membered cyclic carbonates, coupling reactions that involve epoxides and carbon dioxide are ideal. This review introduces environmentally benign catalytic systems for the synthesis of cyclic carbonates under mild reaction conditions. Application of chiral catalysts to the asymmetric synthesis of optically active cyclic carbonates is also discussed.

CONTENTS

1. INTRODUCTION

Cyclic carbonates are known as important building blocks that are used to prepare useful materials.[1] For instance, five-membered cyclic carbonates **1** are widely utilized as electrolytes for lithium ion batteries, as monomers for polymer synthesis, as greener solvents, and as intermediates for fine chemicals.[2] Therefore, the development of practical and environmentally benign methods for the preparation of cyclic carbonates

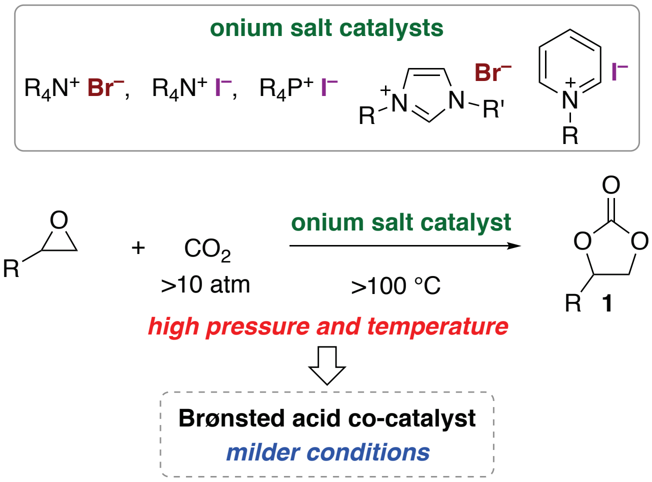
1 is a very important task. The coupling of epoxides and carbon dioxide (CO_2) is recognized as an ideal protocol for the preparation of cyclic carbonates **1** (Scheme 1).[1–3] This synthetic method is an atom-economical process that produces no side products. Most importantly, CO_2 is fixed in organic compounds as cyclic carbonates **1**. For these reasons, catalytic methods for the synthesis of cyclic carbonates **1** from epoxides and CO_2 have been extensively studied, particularly over the past decade. This review focuses on environmentally benign catalytic approaches for the preparation of cyclic carbonates **1** under atmospheric CO_2 pressure.



Scheme 1. Environmentally benign synthesis of cyclic carbonates

2. CATALYSIS OF TETRABUTYLAMMONIUM IODIDE IN THE PRESENCE OF A BRØNSTED ACID CO-CATALYST

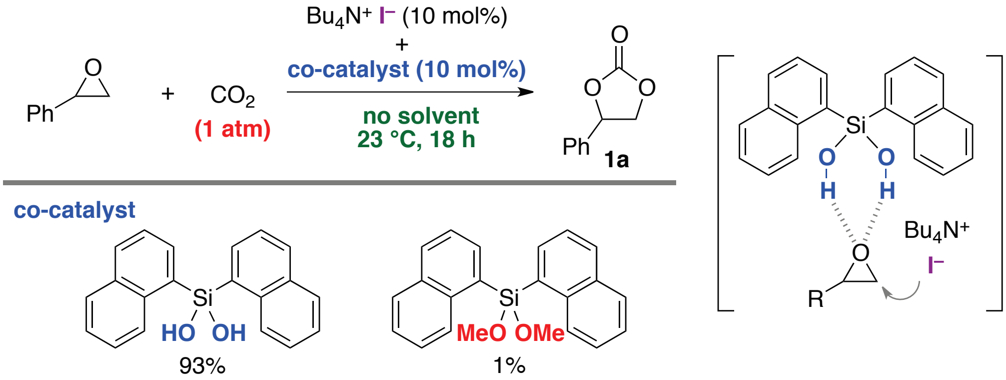
Among the wide variety of catalysts that promote the coupling reactions of epoxides and CO_2, onium salts are attractive as metal-free catalysts for green and sustainable reaction systems.[3] Various commercially available onium halides, such as tetrabutylammonium halides and *N*-alkylpyridinium halides, promote the reactions of epoxides and CO_2 (Scheme 2).



Scheme 2. Onium salt catalysts for cyclic carbonate synthesis

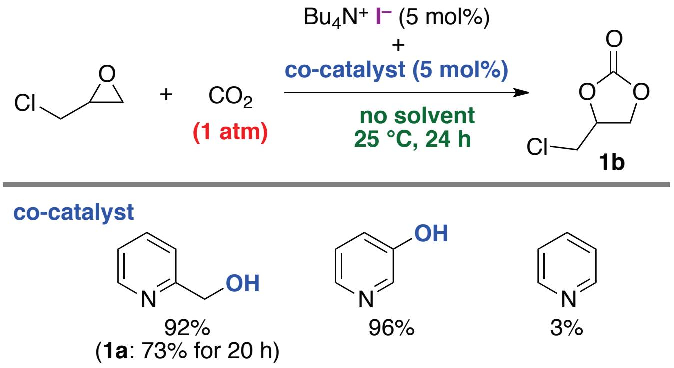
These catalytic systems are environmentally benign methods for the synthesis of cyclic carbonates **1**, albeit with low levels of catalytic activity and these reactions require high levels of CO_2 pressure and temperature. The effects of Brønsted acid co-catalysts, such as alcohols and phenols, have improved the energy consumption of these reaction systems by accelerating the onium halide-catalyzed reactions of epoxides and CO_2. The positive effects of Brønsted acid co-catalysts in the synthesis of cyclic carbonates **1** under milder reaction conditions are well documented.[3,4]

Based on reports of the positive effects of Brønsted acid co-catalysts, Mattson et al. examined the effect of a silanediol co-catalyst (Scheme 3).[5] The reaction of styrene oxide and CO_2 was efficiently promoted by tetrabutylammonium iodide (TBAI)–silanediol binary catalyst under mild reaction conditions. It should be noted that the reaction proceeded under atmospheric CO_2 pressure at room temperature to produce a corresponding cyclic carbonate **1a** in a high yield. To prove the importance of the hydrogen-bonding activation of epoxides, they also examined the effect of a dimethoxysilane co-catalyst. The reaction used a TBAI–dimethoxysilane binary catalyst but proceeded in a sluggish manner, which underscores the importance of hydrogen-bonding activation *via* the use of a silanediol co-catalyst.



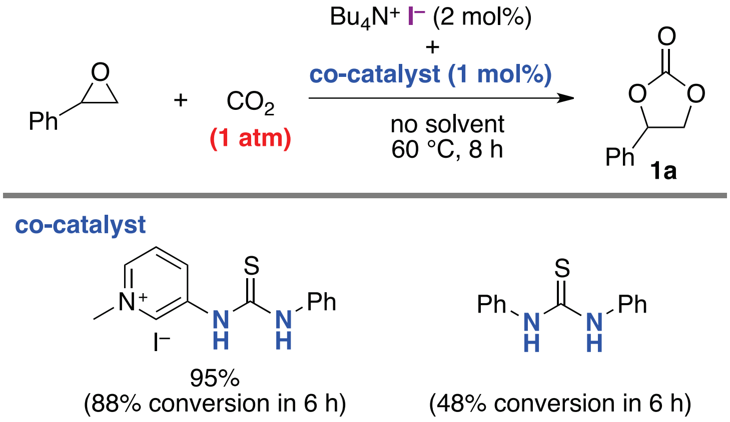
Scheme 3. Effect of a silanediol co-catalyst

Hirose et al. employed other Brønsted acid co-catalysts to achieve the efficient coupling reactions of epoxides and CO_2 under atmospheric pressure at room temperature. They employed 2-pyridinemethanol as a Brønsted acid co-catalyst with TBAI (Scheme 4).[6] A related 3-hydroxypyridine co-catalyst was also effective to produce cyclic carbonate **1b** under mild reaction conditions.[7]



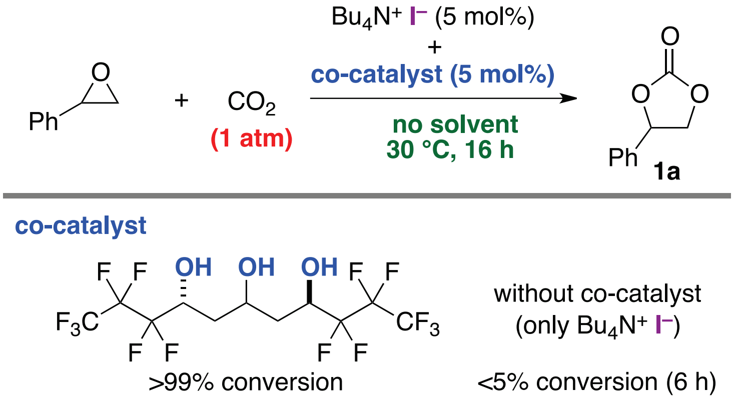
Scheme 4. Effect of pyridinemethanol and hydroxypyridine co-catalysts

Waser, Kass, and co-workers examined other types of Brønsted acid co-catalysts for the synthesis of cyclic carbonates (Scheme 5).[8] They employed a charge-containing thiourea co-catalyst with TBAI. The reaction of styrene oxide under atmospheric CO_2 pressure at 60 °C efficiently proceeded to provide cyclic carbonate **1a** in a high yield. They also discussed the positive effect of a pyridinium moiety on the charged-thiourea co-catalyst and compared this with the catalytic activity of a simple diphenylthiourea co-catalyst.



Scheme 5. Effect of thiourea co-catalysts

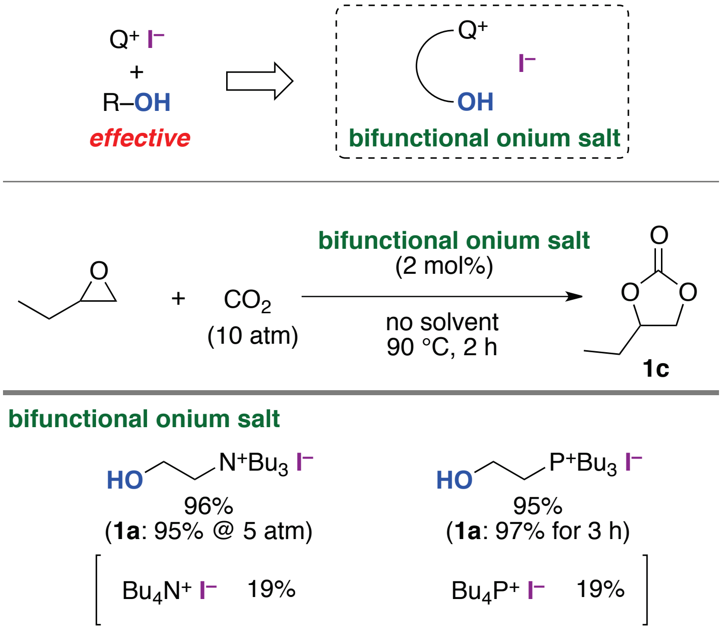
The effect of a fluorinated triol co-catalyst was examined by Quintard and co-workers (Scheme 6).[9] The importance of fluoroalkyl moieties, which increase the acidity of alcohols, on the triol co-catalyst was proven in the reaction of styrene oxide under atmospheric CO_2 pressure at 30 °C.



Scheme 6. Effect of a fluorinated triol co-catalyst

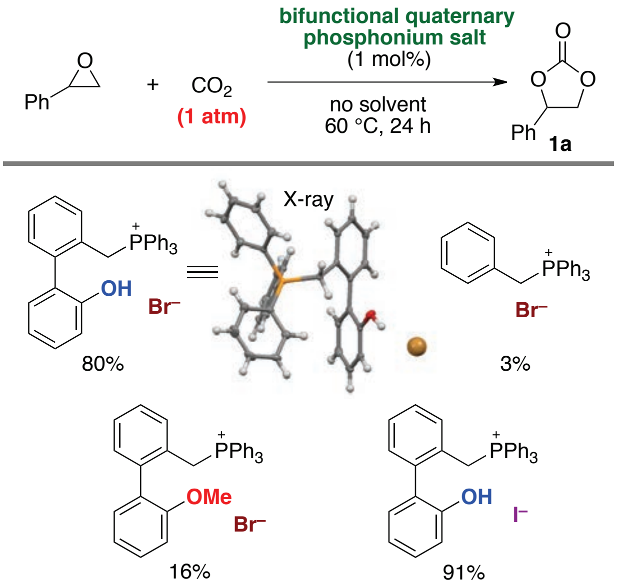
3. BIFUNCTIONAL QUATERNARY ONIUM SALT CATALYSTS

The advantages of a binary catalyst system that uses a quaternary ammonium iodide catalyst and a Brønsted acid co-catalyst were clearly demonstrated in the synthesis of cyclic carbonates from epoxides and CO_2 under mild reaction conditions. Based on these observations, the rational design of bifunctional quaternary onium halides bearing Brønsted acidic moieties seems to be an attractive approach to achieve an efficient catalytic synthesis of cyclic carbonates. Werner et al. reported the effects of bifunctional tetraalkyl-ammonium and -phosphonium iodide catalysts possessing a hydroxy group in the synthesis of cyclic carbonate **1c** (Scheme 7).[10] These bifunctional catalysts clearly showed higher catalytic activities than simple tetrabutyl-ammonium and -phosphonium iodides, although relatively high levels of CO_2 pressure and reaction temperature were required for the reactions.



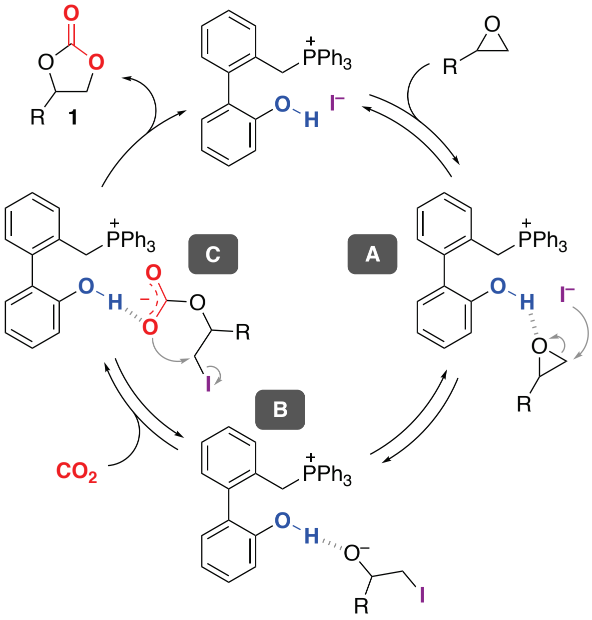
Scheme 7. Initial trial of bifunctional quaternary onium salts by Werner

Our research group has also been interested in the design of bifunctional quaternary phosphonium salt catalysts for the coupling reactions of epoxides and CO_2.[11] We selected a biphenyl backbone for the design of bifunctional quaternary phosphonium salts bearing a phenolic hydroxy group. The catalytic activity of our newly designed bifunctional quaternary phosphonium salt catalysts was examined in the synthesis of cyclic carbonate **1a** (Scheme 8). A mixture of styrene oxide and bifunctional quaternary phosphonium bromide catalyst (1 mol%) was stirred at 60 °C for 24 h under atmospheric CO_2 pressure, and we obtained the target product **1a** in an 80% yield. On the other hand, both the benzyltriphenylphosphonium bromide and the hydroxy group-protecting phosphonium bromide catalyst showed very low reactivities, and the product **1a** was obtained in only low yields (3% and 16% yields, respectively). Based on these results, we concluded that a bifunctional design of our phosphonium salt was essential in the design of effective catalysts. An exchange of the counter-anion from bromide to iodide further improved the catalytic activity to obtain product **1a** in a high yield (91% yield).



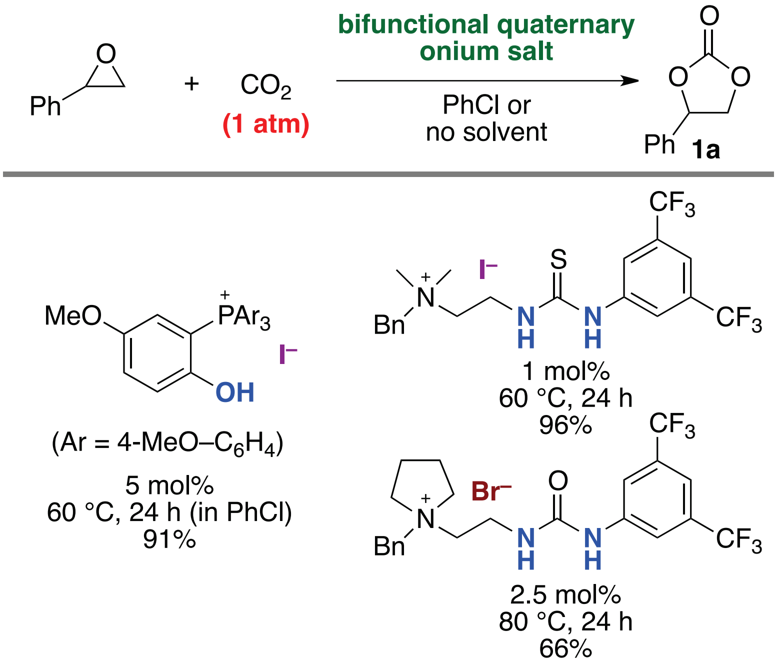
Scheme 8. Bifunctional quaternary phosphonium salts by Shirakawa

The assumed catalytic cycle for the reaction using our bifunctional quaternary phosphonium iodide catalyst was proposed, as shown in Scheme 9. In this reaction, epoxide is activated *via* hydrogen-bonding with a phenolic hydroxy group on the catalyst (intermediate **A**). The activated epoxide then undergoes nucleophilic attack by an iodide counter-anion to form intermediate **B**. The reactive alkoxide in intermediate **B** attacks CO$_2$ to yield intermediate **C**. The intramolecular ring-closing of intermediate **C** affords cyclic carbonate **1** with a regeneration of the bifunctional phosphonium iodide catalyst. The positive effect of the iodide anion in comparison with bromide anion in Scheme 8 can be explained by a lower ability to coordinate with a phenolic hydrogen (intermediate **A**) and by the ability of the higher leaving groups (intermediate **C**).



Scheme 9. Assumed catalytic cycle

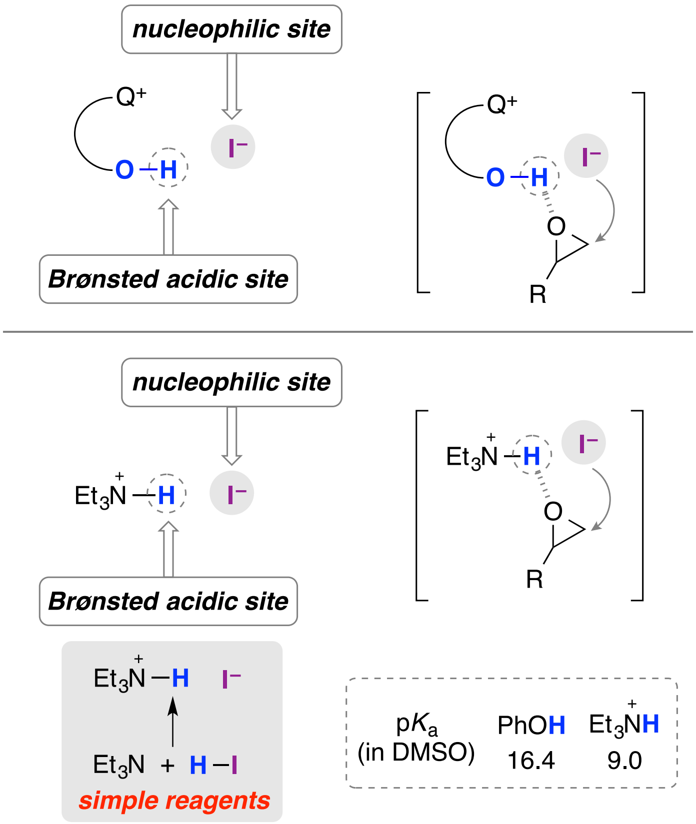
Other research groups also reported the use of different bifunctional quaternary onium halide catalysts for the synthesis of cyclic carbonates (Scheme 10). For example, Toda, Suga, and co-workers examined the catalytic activities of bifunctional tetraarylphosphonium iodides.[12] Waser et al. and Wang et al. independently reported the use of related-bifunctional tetraalkylammonium halide catalysts bearing a thiourea or urea moiety for the synthesis of cyclic carbonate **1a** under atmospheric CO_2 pressure.[13,14]



Scheme 10. Other bifunctional quaternary onium salt catalysts

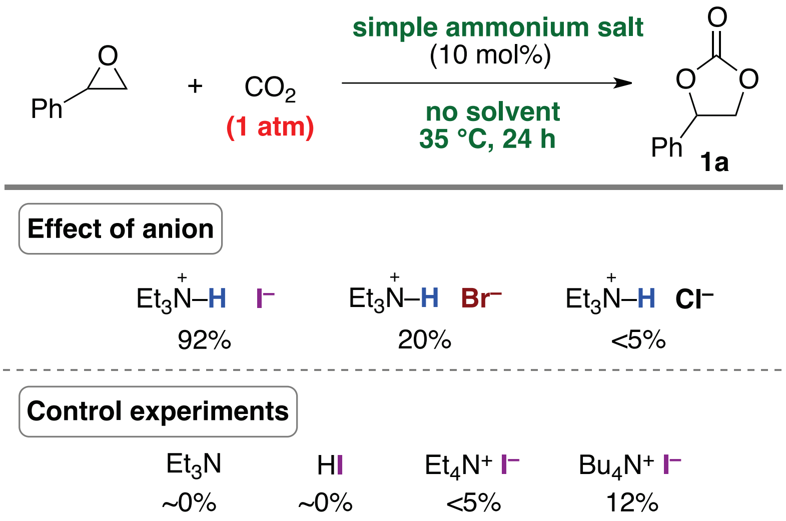
4. SIMPLE AMINE HYDROIODIDES AS BIFUNCTIONAL ONIUM SALT CATALYSTS

Designed bifunctional quaternary onium halide catalysts bearing Brønsted acidic moieties efficiently promoted the coupling reactions of epoxides and CO_2 under atmospheric pressure. The importance of the activation of epoxides by the Brønsted acidic moieties was clearly demonstrated in these reports. The design concept of these effective bifunctional quaternary onium iodides prompted our interest in the catalytic ability of triethylamine hydroiodide as a simple, readily available, and economical catalyst (Scheme 11).[15] The hydrogen on the nitrogen atom of triethylamine hydroiodide is known to possess sufficient acidity to activate epoxides. Thus, triethylamine hydroiodide works as a bifunctional catalyst to promote the coupling reactions of epoxides and CO_2.



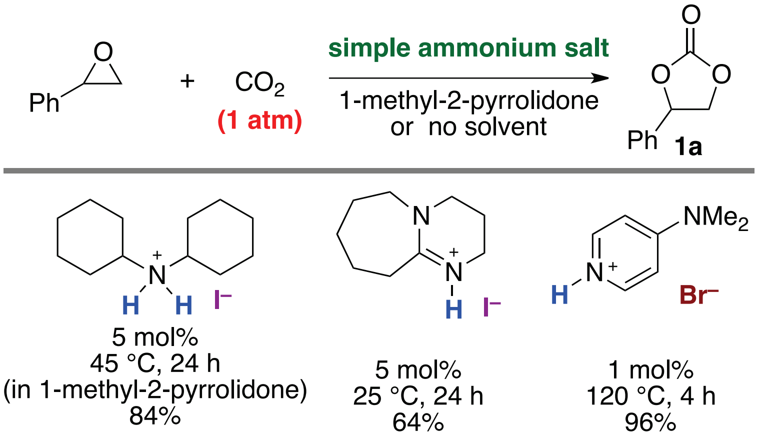
Scheme 11. Triethylamine hydroiodide as a bifunctional ammonium salt catalyst

The catalytic ability of commercially available triethylamine hydroiodide was investigated in the reaction of styrene oxide to produce cyclic carbonate **1a** under atmospheric CO_2 pressure at 35 °C (Scheme 12). The reaction procedure is simple. A mixture of styrene oxide and triethylamine hydroiodide (10 mol%) was stirred for 24 h at 35 °C under a CO_2 atmosphere (1 atm, using a balloon). The resultant reaction mixture was purified by column chromatography on silica gel, and cyclic carbonate **1a** was isolated in a 92% yield. The effect of halide anions was also investigated, and triethylamine hydrobromide and hydrochloride showed significantly lower reactivities (20 and <5% yields, respectively). To clarify the importance of the bifunctional properties of triethylamine hydroiodide, reactions were conducted using either triethylamine or hydroiodic acid. As expected, almost none of the target product **1a** was obtained in these reactions. In addition, the catalytic activities of tetraalkylammonium iodides were also compared with triethylamine hydroiodide. Tetraethylammonium and tetrabutylammonium iodides showed low reactivities under the mild reaction conditions (<5 and 12% yields, respectively). These results clearly indicated that the bifunctional feature of triethylamine hydroiodide was essential to promote the reaction efficiently under mild reaction conditions.



Scheme 12. Effect of ammonium salt catalysts

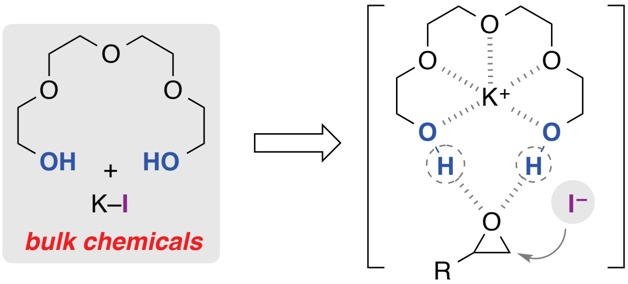
Other simple amine hydro-iodide or -bromide catalysts were also effective in the coupling reactions of epoxides and CO_2 under atmospheric pressure (Scheme 13).[16]



Scheme 13. Other simple ammonium salt catalysts

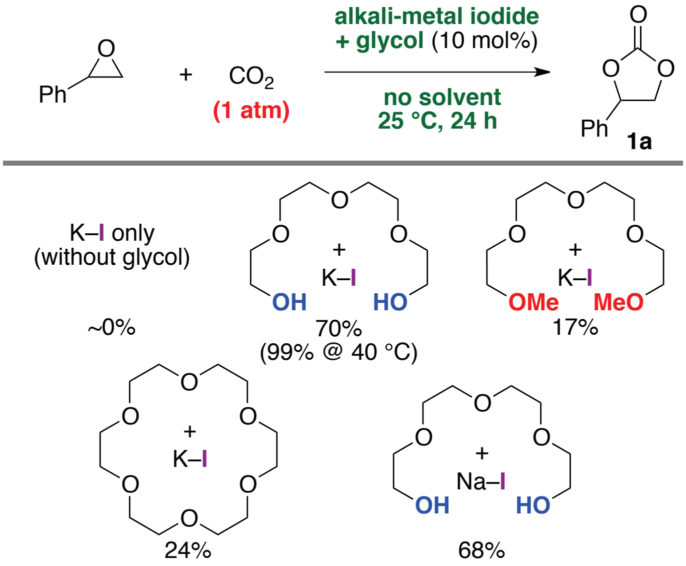
5. POTASSIUM AND CALCIUM IODIDE–GLYCOL COMPLEX CATALYSTS

Simple amine hydroiodides worked as effective catalysts for the synthesis of cyclic carbonates **1** under mild reaction conditions. Based on these findings, we became interested in the catalytic ability of a potassium iodide (KI)–tetraethylene glycol complex as a practical catalyst.[17] Tetraethylene glycol is known to form a complex with potassium salts that significantly increases the nucleophilic ability of iodide anions. Furthermore, the terminal hydroxy groups of tetraethylene glycol activate epoxide substrates *via* hydrogen-bonding interactions (Scheme 14).



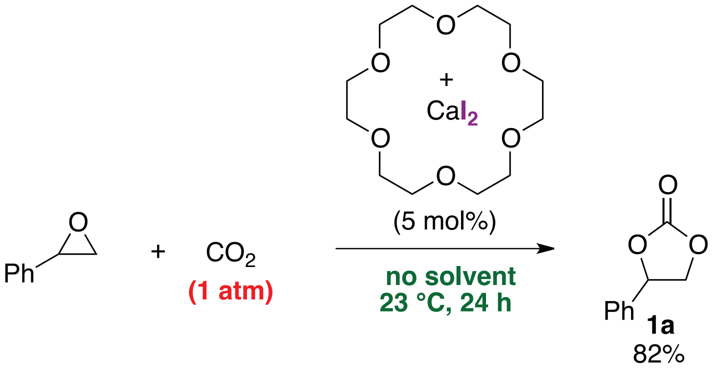
Scheme 14. Potassium iodide–tetraethylene glycol complex as a practical catalyst

The catalytic ability of KI–ethylene glycol complexes was investigated in the reaction of styrene oxide to produce cyclic carbonate **1a** under atmospheric CO_2 pressure at room temperature (Scheme 15). When KI alone was used as the catalyst, almost no reaction was observed. On the other hand, the reaction using KI–tetraethylene glycol complex proceeded smoothly to provide cyclic carbonate **1a** in a good yield (70% yield). Note that the reaction with a KI–tetraethylene glycol complex catalyst at 40 °C gave product **1a** in an almost quantitative isolated yield (99%). To clarify the role of hydroxy groups in tetraethylene glycol, we also examined the reaction with tetraethylene glycol dimethyl ether. As expected, lower catalytic activity was observed in this reaction, which gave product **1a** in a low yield (17% yield). These results clearly indicated that the hydroxy groups of tetraethylene glycol were important for the efficient promotion of the reaction. Additionally, the catalytic activity of an 18-crown-6 complex with KI, which is a known catalyst system for this reaction, was also compared with that of the tetraethylene glycol complex.[18] The 18-crown-6 complex showed reactivity that was inferior to that of the tetraethylene glycol complex (24% vs. 70% yields, respectively). The effect of alkali metal halides was next investigated. A sodium iodide (NaI)–tetraethylene glycol complex catalyst gave results comparable to those of the KI complex.



Scheme 15. Effects of glycols and alkali metal salts

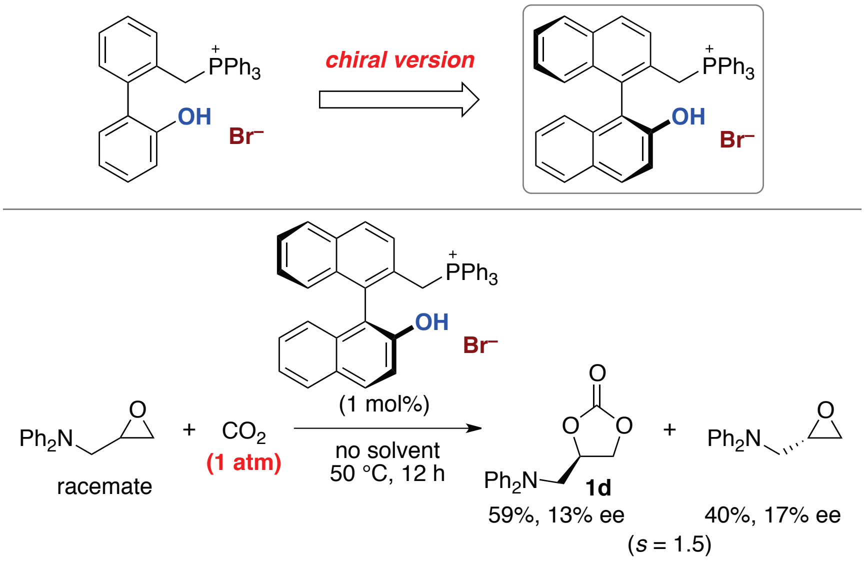
Werner et al. examined the catalytic activity of calcium iodide (CaI_2)–18-crown-6 complex for the coupling reaction of epoxides and CO_2 (Scheme 16).[19] The CaI_2 complex efficiently promoted the reaction of styrene oxide under atmospheric CO_2 pressure at room temperature to provide cyclic carbonate **1a** in a good yield. With this complex catalyst, the calcium worked as a Lewis acid to activate epoxide.



Scheme 16. Calcium iodide–crown ether complex catalyst

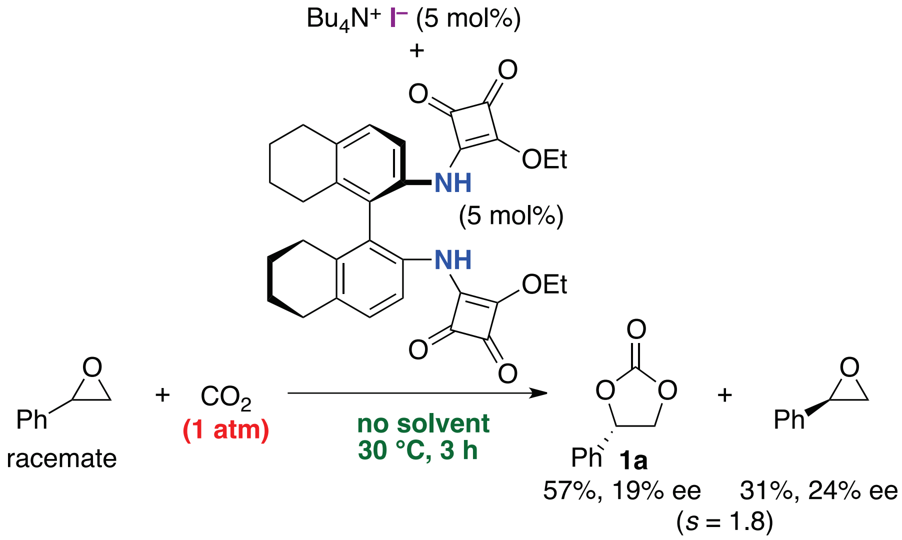
6. CATALYTIC ASYMMETRIC SYNTHESIS OF CYCLIC CARBONATES

Catalytic asymmetric synthesis of chiral cyclic carbonates from epoxide and CO_2 is an attractive and challenging pursuit in modern organic synthesis.[20] Based on the design of our bifunctional quaternary phosphonium salt catalyst with a biphenyl backbone, we prepared a chiral version of the catalyst with an axially chiral binaphthyl backbone (Scheme 17).[11] A chiral bifunctional quaternary phosphonium salt catalyst was applied to the kinetic resolution of epoxide with CO_2. A mixture of the racemic epoxide and chiral catalyst (1 mol%) was stirred at 50 °C for 12 h under a CO_2 atmosphere (1 atm, using a balloon), and cyclic carbonate **1d** was obtained in a 13% ee (59% yield) with recovery of the unreacted epoxide in a 17% ee (40% yield) (s = 1.5). Although the chiral recognition ability of the chiral bifunctional phosphonium salt catalyst was insufficient, this is a first valuable example of an organocatalyzed kinetic resolution for the coupling reaction of epoxide and CO_2.



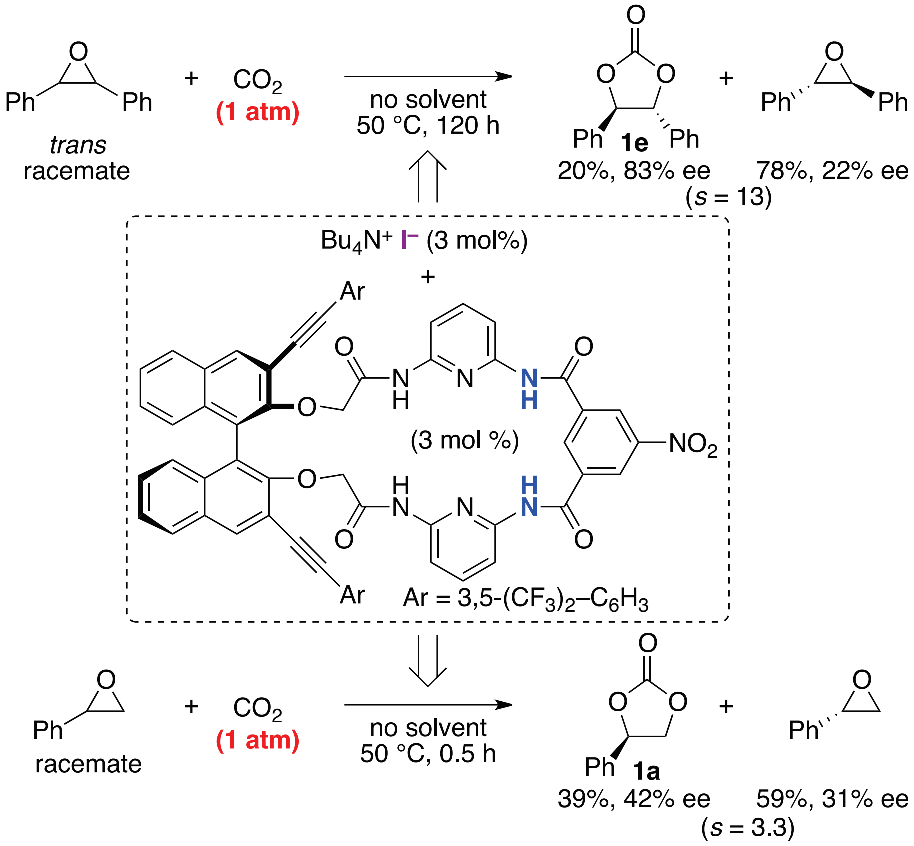
Scheme 17. Chiral bifunctional phosphonium salt for kinetic resolution

Takaishi, Ema, and co-workers examined the kinetic resolution of styrene oxide with CO_2 *via* the use of chiral hemisquaramide as a hydrogen-bonding catalyst in the presence of TBAI (Scheme 18).[21] The TBAI–chiral hemisquaramide binary catalyst efficiently promoted the kinetic resolution under atmospheric CO_2 pressure to provide cyclic carbonate **1a** in moderate selectivity (s = 1.8).



Scheme 18. Kinetic resolution with chiral hemisquaramide

Ema et al. also reported the effect of a chiral macrocyclic hydrogen-bonding catalyst in the kinetic resolution of epoxides with CO_2 (Scheme 19).[22] The kinetic resolution of racemic *trans*-stilbene oxide was promoted by TBAI–chiral macrocycle binary catalyst under atmospheric CO_2 pressure. After the reaction for 120 h at 50 °C, cyclic carbonate **1e** was obtained with good selectivity (s = 13). This catalytic asymmetric system was also applied to the kinetic resolution of styrene oxide.



Scheme 19. Kinetic resolution with a chiral macrocycle

7. CONCLUSION

The environmentally benign synthetic methods of five-membered cyclic carbonates were summarized in this review.[23] Onium iodide–Brønsted acid binary catalyst systems realized efficient coupling reactions of epoxides and CO_2 under mild reaction conditions (atmospheric CO_2 pressure at room temperature). Based on these findings, bifunctional onium iodide catalysts bearing Brønsted acidic functionalities were designed for application to cyclic carbonate synthesis under mild reaction conditions. Although several catalytic systems have realized this reaction under atmospheric CO_2 pressure at room temperature, improvements in the turnover frequency (TOF) and catalyst loading are still required to construct practical and environmentally benign reaction systems. Limited examples of the kinetic resolution of racemic epoxides with CO_2 were also introduced. The development of highly effective chiral catalysts for this kinetic resolution remains a challenging project.

ACKNOWLEDGEMENTS

A portion of the research by our group on this topic was supported by the Tokyo Kasei Chemical Promotion Foundation, by The Kurata Grants from The Hitachi Global Foundation, and by the Asahi Glass Foundation.

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