



Catalytic, kinetic and mechanistic insights into the fixation of CO₂ with epoxides catalyzed by phenol functionalized phosphonium salts

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	Supporting information for this article is given via a link at the end of the document.						
Abs	tract: A series of hydroxyl functionalized phosphonium salts were	Promising transformations even on an industr					

studied as bifunctional catalysts for the conversion of CO₂ with epoxides under mild and solvent-free conditions. The reaction in the presence of a phenol-based phosphonium iodide proceeded via a first order rection kinetic with respect to the substrate. Notably, in contrast to the aliphatic analogue the phenol-based catalyst showed no product inhibition. The temperature dependence of the reaction rate was investigated and the activation energy for the model reaction was determined from an Arrhenius-plot ($E_a = 39.6 \text{ kJ mol}^{-1}$). The substrate scope was also evaluated. Under the optimized reaction conditions, 20 terminal epoxides were converted at room temperature to the corresponding cyclic carbonates which were isolated in yields up to 99%. The reaction is easily scalable and was performed on a scale up to 50 g substrate. Moreover, this method was applied in the synthesis of the antitussive agent dropropizine starting from epichlorohydrin and phenylpiperazine. Furthermore, DFT calculations were performed to rationalize the mechanism and the high efficiency of the phenol-based phosphonium iodide catalyst. The calculation confirmed the activation of the epoxide via hydrogen bonding for the iodide salt which facilitates the ring-opening step. Notably, the effective Gibbs energy barrier regarding this step is 97 kJ·mol⁻¹ for the bromide and 72 kJ·mol-1 for the iodide salt which explains the difference in activity.

Introduction

The use of CO₂ as a C1 building block is receiving increasing attention from the scientific and industrial community due to economic and ecological considerations.^[1] It is progressively regarded as an attractive, inexpensive and abundant renewable feedstock rather than waste.^[2] Furthermore, in a future CO₂ based circular economy it can be used as a platform to produce bulk chemicals and energy carrier through its transformation to fuels.^[3] Nevertheless, due to its thermodynamic stability, the efficient activation and chemical fixation is still challenging.^[4] This can be partially overcome by converting CO₂ with high energy starting materials such as epoxides or hydrogen in the presence of a catalyst. Thus, it is crucial to develop new catalytic processes that allow the efficient transformation of CO₂ into valuable products.

Promising transformations even on an industrial scale are the fixation of CO₂ into organic carbonates or polycarbonates (Scheme 1, A).^[1b, 5] These processes can be of significant advantage regarding economic and ecological considerations e.g. by saving fossil resources or lowering the carbon footprint of a process.^[6]

A) Conversion of epoxides with CO₂



B) Concepts for the activation of epoxides in cyclic carbonate synthesis



C) Bifunctional phosphonium salt catalysts



Scheme 1. Synthesis of cyclic and polycarbonates as well as concepts and selected catalysts for the conversion of epoxides with CO₂.

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The synthesis of five-membered cyclic carbonates **2** from CO_2 and epoxides **1** is of particular interest. It is an atom economic reaction and excellent example for green chemistry.^[7] Moreover, cyclic carbonates are important materials which are used in various applications, e.g. as intermediates in organic synthesis,^[8] indirect CO_2 reductions to methanol,^[9] green solvents,^[10] electrolyte in lithium ion batteries,^[11] polymer building blocks^[12] and even as additives in drugs and cosmetics.^[13]

Metal-based systems including Al-salen^[14] and triphenolat^[15] complexes have been reported for the synthesis of cyclic carbonates.^[16] In these binary catalytic systems, the Lewis acidic metal complexes are often combined with an external nucleophile typically a halide ion from an onium salt to activate the epoxide (Scheme 1, B). The nucleophilic counter anion of the salt acts as a temporary relay, ring opening the epoxide, which is activated by the Lewis acidic metal center, and subsequently serving as a leaving group upon ring closure after CO₂ insertion. Catalytic systems that operate under near-ambient conditions (low CO2 pressure and room temperature) are of interest in terms of advances to wards sustainability.^[17] In the past decade, the use of organocatalysts has attracted increasing attention in this research area.^[18] A significant benefit of this catalyst class is undoubtedly the metal-free carbon-based scaffold which is associated with a high potential for structural modification, catalyst tuning and immobilization.^[19] In analogy to the metal-based systems, the combination of hydrogen bond donors and quaternary ammonium salts to activate the epoxide proved to be a promising concept in the field of organocatalyzed cyclic carbonate synthesis (Scheme 1. B).^[20] Systems based on different hydrogen bond donor functionalities, e.g. alcohols.^[21] carboxylic acids.^[22] silanol.^[23] phenols^[24] and (thio-)ureas^[25] were used in combination with external nucleophiles to catalyze the addition of CO₂ to epoxides to yield the corresponding cyclic carbonates. Even though great advances have been made it is still challenging to realize this reaction efficiently under low CO₂ pressures (1 atm) and reaction temperatures <100 °C.[17]

It is generally recognized that bifunctional catalysts consisting of an electrophilic group and an internal nucleophile significantly accelerate the process through synergistic effects.^[18, 26] However, it was not until recently that bifunctional phosphonium salts emerged as potent class of organocatalysts (Scheme 1, C). In 2014 our group reported the use of bifunctional phosphonium salt catalyst 3 bearing an alcohol moiety as hydrogen bond donor. This catalyst allowed for the synthesis of cyclic carbonates at 90 °C and 1.0 MPa CO₂ pressure yielding the desired products in up to 99% yield under solvent-free conditions.^[27] More recently we reported a mechanistic study on the use of bifunctional phosphonium salt 3.^[26a] This study clearly showed that the epoxide is activated by hydrogen bonding and that the order of reactivity in regard to the anion increased in the order Cl⁻ < Br⁻ < I[−]. Significantly, the analysis of the kinetic data revealed that partial product inhibition hampered the overall efficiency of this catalyst. Also in 2014, Sheng-lian et al. introduced carboxylic acid derivative 4 as a catalyst for the synthesis of cyclic carbonates at elevated temperatures and pressure (130 °C and 2.5 MPa). [28] In 2016, Shirakawa et al. showed that biphenyl-derived phosphonium salt 5 enables the conversion of epoxides with CO2 at 60 °C and low CO2 pressure (1.0 atm).^[29] In the same year, Toda and Suga studied bifunctional tetraarylphosphonium salt 6 which allowed for the synthesis of cyclic carbonate at atmospheric CO₂ pressure but high reaction temperatures of 120 °C in chlorobenzene as the solvent.^[30] Very recently, they carefully investigated the impact of the electronic properties of the substituents on the catalyst efficiency.^[31] The introduction of electron-donating groups significantly enhanced the catalytic activity which allowed to reduce the reaction temperature to 60 °C. In 2017 our group reported the use of bifunctional phenolic phosphonium bromide **7** for the preparation of oleochemical carbonates at 80 °C and 2.5 MPa CO₂ pressure.^[32] Based on our previous results we envisioned that the corresponding iodide **8** should show superior efficiency as catalyst in the synthesis of cyclic carbonates under mild and solvent free-conditions. Herein we report the synthesis and application of this catalyst as well as a thorough kinetic investigations and DFT calculations to rationalize its superior performance and the reaction mechanism.

Results and Discussion

Catalyst screening

We chose the conversion of 1,2-butylene oxide (1a) with CO₂ to produce 1,2-butylene carbonate (2a) as a benchmark system to evaluate and compare to previously reported catalysts under uniform reaction conditions (Table 1). Our 1st generation bifunctional phosphonium salts 3 (2 mol%) gave the desired product 2a in 25% yield after 24 h at 23 °C and 1.0 MPa CO₂ pressure (Table 1, Entry 1). In the presence of catalysts 5, 6 and 7 significantly lower conversions and yields \leq 10% were achieved (Entries 2–4). In contrast phosphonium iodide 8 gave 2a in 65% yield (Entry 5).

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	~ .	+ co. <u>-</u>	2 or 5 mol% catalyst 23–90 °C, 2–24 h p(CO ₂)= 0.1 or 1.0 MPa solvent-free			
	Et 1a	p(C				
Entry	Catalyst	x / mol%	T/ °C	<i>t</i> / h	Yield/ % ^a	TON
1	3	2	23	24	25	13
2	5	2	23	24	2	1
3	6	2	23	24	2	1
4	7	2	23	24	10	5
5	8	2	23	24	65	33
6	7	2	45	6 (24)	60 (>99)	30
7	8	2	45	6 (24)	85 (>99)	43
8	7	2	90	2	89	45
9	8	2	90	2	96	48
10	8	5	23	24	>99	50
11 ^b	8	5	23	24	71	36

Table 1. Comparison of bifunctional phosphonium salts in the cycloaddtion of CO_2 with epoxides.

Reaction conditions: 1.0 equiv **1a** (1.00 g, 13.9 mmol), 2–5 mol% catalyst, 2–24 h, $p(CO_2)$ = 1.0 MPa, solvent-free. ^aYields were determined by ¹H NMR using mesitylene as internal standard. ^b $p(CO_2)$ = 0.1 MPa.

This is remarkable since catalyst **7** was identified to be more efficient compared to **8** at higher temperature (100 °C) and CO_2 pressure (5.0 MPa) in the synthesis of oleochemical

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carbonates.^[32] With increasing reaction temperature the obtained yield for **2a** equalizes (Entries 6–9). Notably, in the presence of 5 mol% **8** an excellent yield >99% was achieved at 23 °C. Even at a lower CO₂ pressure of 0.1 MPa **2a** was obtained in 71% yield (Entries 10 and 11). The lower yield might be due to a lower CO₂ concentration in solution at this pressure which can have a strong impact on the reaction rate.^[33]

Kinetic investigations

The efficiency of bifunctional phosphonium salts is closely related to the ability of activating the epoxide by hydrogen bonding.^[20] Recently, we reported a detailed mechanistic study on alkyl bridged bifunctional phosphonium salts as catalysts in cyclic carbonate synthesis.^[26a] In this study the activation of epoxide 1a by hydrogen bonding to catalyst 3 was proven by IR spectroscopy. Moreover, kinetic and IR studies revealed an interaction of 3 with the product 2a leading to significant product inhibition. In the present case attempts failed to investigate the interaction of phenolic catalyst 8 with the epoxide or the carbonate by transmission IR-spectroscopy due to an overlap of the OHstretching vibration from the phenol moiety with bands of the C-H stretching modes. Unfortunately, also measurements in the ATR-mode did not provide un ambiguous results in this regard.^[34] However, to further investigate the difference in the activity of catalysts 3 and 8. we performed kinetic measurements of the model reaction with 1.2-butylene oxide (1a) as the substrate at 23 °C and 45 °C. These experiments have been conducted at a CO₂ pressure of 1.0 MPa with a substrate content of 460 mmol and 2 mol% of catalyst. Product formation was monitored by the sampling of the liquid reaction mixture at distinct time intervals followed by ¹H NMR spectroscopic an alyses. The selectivity of 2a was consistently >99%. At 23 °C with 8 as a catalyst, an induction period was observed which was addressed to the low solubility of 8 in the pure epoxide at room temperature.^[34] For the catalyst system 3, no induction period has been identified but at higher conversions the catalytic performance is significantly lower compared to the phenolic catalyst 8. In the next step, we performed these model reactions at 45 °C. Now, for the catalyst 8, the yield-vs-time data can be described by a first-order kinetic model (Equation 1) as shown in Figure 1.



Figure 1. Comparison of a first-order kinetic fit and the kinetic model represented in equation 2 for the conversion of epoxide **1a** with CO₂ in the presence of catalyst **3** and **8**. The observed selectivity was >99%. Reaction conditions: 1,2-butylene oxide (**1a**, 460 mmol), 2 mol% catalyst **3** or **8**, $p(CO_2) = 1.0$ MPa, 45 °C, 48 h.

In contrast, for the reaction in the presence of **3** a kinetic model in which product inhibition was considered needs to be used (Equation 2). This equation is based on a Michaelis–Menten model including a reversible product inhibition which is valid for the case of a first-order with respect to the substrate. The equilibrium constant K_{inh} of the product inhibition with the aliphatic catalyst **3** was calculated as 0.260 L mol⁻¹. The fact that the yield-vs-time data for **8** was best described with the first-order model indicates that product inhibition is not relevant for this system. The obtained observable rate constants k^{obs} were $0.197 h^{-1}$ (**8**) > $0.0605 h^{-1}$ (**3**) reflecting the catalytic activity.^[34] From these observations it can be concluded that both, the absence of a significant product inhibition and an intrinsically higher activity for the catalytic system with catalyst **8** causes its better performance.

$$\frac{dY}{dt} = k^{obs}(1 - Y)$$
(Eq. 1)
$$\frac{dY}{dt} = \frac{k^{obs}(1 - Y)}{1 + K_{inh}[S]^{0}Y}$$
(Eq. 2)

We were further interested in the temperature dependence of the reaction rate for the catalytic system with the phenolic catalyst 8.^[34] Therefore, additional experiments have been performed so that a temperature range of $\theta = 35 - 90 \,^{\circ}\text{C}$ was covered. Yield vs time data was analyzed using a first-order kinetic model (firstorder with respect to the substrate concentration) providing observable rate constants (k^{obs}). An acceptable Arrhenius behavior was found between θ = 35-65 °C (T = 308.15-338.15K). Interestingly, at higher temperatures the values of the rate constant decreased which might be addressed to a change in the solubility of CO2 at higher temperatures.^[33b] From an Arrhenius-plot a value for the activation energy was calculated with $E_a = 39.6 \text{ kJ} \cdot \text{mol}^{-1}$ which is in agreement with previous reports (Figure 2).^[35] A respective Eyring-plotallowed for the calculation of the enthalpy of activation which gave a value of $\Delta H^{\ddagger} = 36.9 \text{ kJ} \cdot \text{mol}^{-1}.$



Figure 2. Arrhenius-plot for the estimation of the activation energy E_a of the conversion of epoxide **1a** with CO₂ in the presence of catalyst **8** over the temperature range of θ = 35 - 65 °C (*T* = 308.15 - 338.15 K). Reaction conditions: 1,2-butylene oxide (**1a**, 460 mmol), 2 mol% catalyst **8**, *p*(CO₂) = 1.0 MPa. y = -476.5x + 13.277, R² = 0.9638.

Substrate scope

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Due to the observed superior efficiency of catalyst 8 we evaluated the substrate scope regarding the conversion of terminal epoxides 1 to the respective cyclic carbonates 2 at room temperature (Table 2). Carbonates 2a-d bearing aliphatic substituents were synthesized in good to excellent yields. Particularly, propylene carbonate (2b) has attracted much interest due to its applications as an electrolyte in lithium ion batteries[11] and is regarded as one of the most sustainable alternative solvents in organic chemistry.^[10a] Notably, the conversion of enantiomerically pure S-propylene oxide (S-1b) led to the corresponding cyclic carbonates S-2b in 94% yield and >99% ee. Due to the lower polarity of epoxide 1c and 1d the solubility of the catalyst was reduced and the addition of a solvent (nBuOH) was required to achieve 95% and 72% yield for 2c and 2d, respectively. The phenyl substituted product 2e was isolated in a yield of 74%. In this case acetophenone was found as a by-product which was derived from a Meinwald rearrangement.^[36] This indicates that the conversion of styrene oxide (1e) proceeds at least partially via a cationic intermediate. This assumption is supported by the partial racemization which was observed when R-styrene oxide (R-1e) was converted. In this case carbonate R-2e was isolated in 74% yield and 83% ee. Furthermore, epichlorohydrin (1f) was converted to the respective carbonate 2f in an excellent yield of 95% while morpholine derivative 2g was obtained in 73% yield. After having established a general protocol for the conversion of monosubstituted epoxides under mild conditions, the catalyst system was applied in converting disubstituted terminal epoxides. Products 2h and 2i were obtained in yields of 86 and 85%, respectively, even though elevated reaction temperature (80 °C) and higher CO₂ pressure (2.5 MPa) were required.





Reaction conditions: 1.0 equiv 1 (1.00 g), 5 mol% 8, 23 °C, 24 h, $p(CO_2)=1.0$ MPa, solvent-free. Isolated yields are given. ^a*n*-Butanol was employed as a solvent. ^bYield were determined by ¹H NMR using mesitylene as internal standard. ^c80 °C, $p(CO_2)=2.5$ MPa.

Cyclic carbonates are frequently used as protecting groups for 1,2-diols.^[37] The successful preparation of morpholine derivative **2g** prompted us to evaluate the synthesis of dropropizine *rac-***10**, which is an antitussive agent typically employed as a racemic mixture in a number of commercial cough suppressant.^[38] In general, it is prepared from the epoxides **1j** under acidic conditions or by direct amination of solketal, a 1,2-hydroxy-protected derivative of glycerol, via ruthenium-catalyzed hydrogen borrowing reaction and subsequent ketal hydrolysis.^[39] The intermediate epoxide *rac-***1j** as well as enantiomerically pure *R*- and *S-***1j** are obtained in yields up to 96% from

phenylpiperazine (9) and the respective epichlorohydrin (1f) (Scheme 2). The subsequent conversion under the standard reaction conditions for terminal epoxides gave the respective carbonate rac-2j in 65% after 48 h. At 45 °C full conversion was achieved and 2j was isolated in >99% yield. The subsequent cleavage of the carbonate protecting group under basic conditions gave dropropizine rac-10 in 95% yield. Notably, the formation and subsequent cleavage of the carbonate to obtain dropropizine in a sequential one-pot reaction could also be achieved leading to rac-10 in 61% yield. We envisioned that also enantiomerically pure dropropizine should be accessible via this route. Notably, this protocol circumvents the acidic hydrolysis of the epoxide to the 1,2-diol which might lead to racemization. The precursor R-1j and S-1j were readily accessible from R- and Sepichlorohydrin (R- and S-1f) and amine 9 in excellent yields and enantioselectivities of 94% (98% ee) and 95% (97% ee), respectively. The conversion of R-1j with CO2 at 45 °C led to carbonate R-2j in excellent 90% yield. However, under these conditions partial racemization was observed and R-2j was obtained in 24% ee. Thus, S-2h was converted at lower temperature (23 °C) which led to a significant improvement to 54% ee but a lower yield of 61%. The deprotection of carbonates R-2j and S-2j occurred stereoselectively as expected to yield enantiomerically enriched R-10 and S-10 in 95% and 99% yield, respectively.



Scheme 2. Synthesis of dropropizine via cyclic carbonate **2j**. Reaction conditions: i) 23 °C, 1 h, H₂O then NaOH/H₂O, 75 °C, 15 min. ii) 5 mo% **8**, 23 °C, 48 h, $p(CO_2)$ = 1.0 MPa. iii) NaOH/H₂O, 3 h, 23 °C. ^a45 °C. ^b45 °C, 24 h

As the major by-product in the manufacturing of biodiesel, glycerol is widely available.^[40] Thus, the use of glycerol as the feedstock for the preparation of value-added products is an attractive goal. Moreover, the use of this biobased material can lead to a significant reduction in the carbon footprint, e.g. in the synthesis of carbonates, compared to their production from fossil resources.[6a] Glycidol (11c) and its derivatives can be obtained from glycerol.^[41] The respective carbonates show unique properties and find a range of applications e.g. as synthetic building blocks, monomers and solvents.^[10b, 42] Hence, we were particularly interested in the preparation of cyclic carbonates 12aj from epoxides 11a-j in the presence of catalyst 8 (Table 3). Under the standard conditions the conversion of glycidyl ethers 11a and 11b did not lead to full conversion and 12a and 12b were isolated in 56 and 58% yield, respectively. Hence, we adjusted the reaction time to 48 h which led to full conversion and excellent isolated yields of 96 and 97%. The conversion of glycidol (11c)

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which is susceptible to polymerization^[43] gave glycerol carbonate 12c in 82%. In addition, the highly fluorinated carbonates 12d and 12e, which can be used as electrolytes in lithium batteries, [44] were prepared in yields of 86% and 79% respectively. Furthermore, the unsaturated carbonates 12f and 12g which are potential building blocks for homo- and copolymers with a cyclic carbonate units in the backbone were isolated in distinguished yields up to 99%. [45] Epoxide 11h containing a furfuryl moiety can also be synthesized from renewables^[46] and the respective carbonate was isolated in 97% yield. Silyl-functionalized carbonates are often used as precursors for the synthesis of nonisocyanate polyhydroxyurethane hybrid materials.^[47] They also find applications in industry due to their potential utilization as electrolytes^[48] and in surface modification. Thus, we converted **11i** with CO₂ in the presence of catalyst 8 and were able to obtain 12i in 93% under slightly modified conditions. Additionally, bisphenol diglycidyl ether (11j) was converted into the respective carbonate 12j in 95% yield. This biscarbonate is a frequently used monomer for the synthesis of non-isocyanate polyurethanes (NIPUs).[49]

 $\label{eq:table_transform} \begin{array}{l} \textbf{Table 3.} \\ \textbf{Substrate scope for the conversion of glycidol and its derivatives 11} \\ \textbf{into the corresponding carbonates 12}. \end{array}$



Reaction conditions: 1.0 equiv **11** (1.00 g), 5 mol% **8**, 23 °C, 48 h, $p(CO_2)=1.0$ MPa, solvent-free. Isolated yields are given. ^a24 h. ^b2 mol% **8**, 90 °C, 4 h. ^c10 mol% **8**, 45 °C, *n*-butanol was employed as a solvent.

The synthesis of internal carbonates derived from epoxides and CO₂ is rather challenging and is often marginally studied in the evaluation of the substrate scope. Considering the high efficiency of catalyst 8 in the conversion of terminal epoxides under mild conditions we were interested in its performance regarding the conversion of internal epoxides 13 (Table 4). Initially, the standard protocol (5 mol%, 23 °C, 24 h, p(CO₂)= 1.0 MPa) was tested for the conversion of cyclohexene oxide (13a). Under these conditions <10% of the desired carbonate 14a was obtained. Hence, the reaction temperature and CO₂ pressure were increased to 80 °C and 2.5 MPa, respectively. This led to significant improvement of the yield and 14a was obtained in 59%. Moreover, the conversion of epoxides 13b and 13c led to the corresponding cyclic carbonates 14b and 14c in 72 and 82% yield, respectively. Notably, the conversion of cis-stilbene oxide (13d) gave trans-stilbene carbonate trans-14d in a selectivity of 99%. This indicates that the reaction proceeds via a cationic

intermediate (S_N 1-pathway) which is stabilized by the phenyl substituent.^[34] This pathway leads to the thermodynamically more stable *trans*-product. Moreover, 1, 2-diphenyl-ethan-1-one was observed as a by-product, which comes from the Meinwald rearrangement.^[36] In contrast the conversion of *cis*-**13e** and *cis*-methyl oleate (**13f**) gave the respective carbonates in yields up to 84% with a *cis*- to *trans*-selectivity of 25:75. This can be addressed to the less pronounced stabilization of the cationic intermediateby hyperconjugation in the S_N1-pathway.

 Table 4. Substrate scope for the conversion of internal epoxides 13 into the corresponding carbonates 14.



Reaction conditions: 1.0 equiv **13** (1.00 g), 5 mol% **8**, 80 °C, 24 h, $p(CO_2 = 2.5 \text{ MPa}$, solvent-free. Isolated yields are given. ^a*n*-Butanol was employed as a solvent. ^b23 °C, $p(CO_2) = 1.0 \text{ MPa}$. °Yields were determined by ¹H NMR using mesitylene as the internal standard.

DFT calculations

On the basis of our findings and previous reports^[50] we propose a three-step mechanism. The initial step is the ring-opening of epoxide 1a. Subsequently, the positively charged carbon atom of CO2 couples with the negatively charged oxygen atom to form a linear carbonate; alternatively, this step can also be considered as a nucleophilic attack of the negatively charged oxygen atom to the LUMO of CO2. Finally, an intramolecular nucleophilic substitution leads to the formation of the desired cyclic carbonate and liberates the catalyst. Since the nucleophilic counterion has been found to have an important effect on the activity of the catalyst, both bromide salt 7 and iodide salt 8 were considered. On the basis of this proposal, we calculated the full Gibbs free energy surface for the phenol-derived phosphonium halides 7 and 8 catalyzed cycloaddition of CO₂ to epoxide 1a, affording the fivemembered cyclic carbonate 2a. All computational details are given in the Supporting Information. Here we present the results for the more active catalyst 8 while those for the less active bromide salt 7 can be found in the Supporting Information. The optimized structure I shows a hydrogen bonding (2.297 Å) interaction between the phenolic OH and the I⁻ counter ion. Notably, this interaction can also be seen in the crystal structure of catalyst 8 (Figure 3, O1A—H1A…I1Aⁱ: O1A—H1A = 0.89(5) Å, H1A…I1Aⁱ = 2.48(5) Å, O1A…I1Aⁱ = 3.365(3) Å, O1A—H1A…I1Aⁱ $= 172(4)^{\circ}$, symmetry code: (i) -1/2+x,y,1/2-z).

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Figure 3. Molecular structure of catalyst **8** in the solid state. Displacement ellipsoids correspond to 30% probability. Lower occupancy sites are omitted for clarity. The intermolecular hydrogen bond is shown as dashed line.^[51]

For catalyst **8**, two possible pathways for the ring-opening at the methylene (C_{β} , Scheme 3, right) and methine carbon (C_{α} , Scheme 3, left) in the epoxide function were evaluated.



Scheme 3. Intermediates of the calculated catalytic cycle for ring-opening at the methylene (C_{g} , right) and methine carbon (C_{g} , left) at epoxide 1a.

The structure of the intermediates in the catalytic cycle are shown in Scheme 3 while for clarity the optimized structures of transition states **TS1-** α to **TS3-** α as well as **TS1-** β to **TS3-** β are shown separately in Figure 4. The corresponding Gibbs free energy profile for the opening at C_{α} and C_{β} is depicted in Figure 5. The initial step is the epoxide coordination to the phenol-derived phosphonium salt to form intermediate **II** via hydrogen bonding. The coordination is exergonic by 3 kJ·mol⁻¹. This energy difference indicates dynamic equilibrium in favor of **II** (77%). The next step is the nucleophilic attack of I⁻ to the carbon of epoxide with C–O bond cleavage and the formation of a C–I bond.



Figure 4. Optimized structures for transition states of TS1- α to TS3- α as well as TS1- β to TS3- β .

Notably, the ring-opening at C_{β} via transition state of **TS1-** β has an energy barrier of 68 kJ·mol⁻¹ which is lower than that at C_{α} via transition state of **TS1-** α by 20 kJ·mol⁻¹. This can be addressed to the steric interaction as estimated on the basis of the distortion energy of epoxide. Namely, the geometrical strain energy ΔE_{strain} of **1a** in **TS1-** β is 30.6 kJ·mol⁻¹ lower than that in **TS1-** α . The proton of the phenol group is transferred to the oxygen of iodo butan olate forming an ylide and iodo-butanol. The formation of III from II is endergonic by 15 and 9 kJ·mol⁻¹ for 2-iodobutan-1-ol (III- α) and 1-iodobutan-2-ol (III- β), respectively. The co-adsorption of CO_2 from III- α and III- β to form IV- α and IV- β is also endergonic by 14 and 26 kJ·mol⁻¹, respectively. The energy barrier of C-O coupling via transition state of TS2- α and TS2- β is 40 and 57 kJ·mol⁻¹ from III- α and III- β , respectively. The formation of 2iodobutyl carbonate anion V- α and 1-iodobutan-2-yl carbonate anion $V-\beta$ in which O_b is interacting with the OH of phenol is endergonic by 2 and 9 kJ·mol⁻¹ from III- α and III- β , respectively.



Figure 5. Calculated Gibbs free energy profile for the addition of CO_2 to epoxide 1a in the presence of catalyst 8 for the reaction at the methylene (C_β) and methine carbon (C_α).

For the last step (the ring-closure reaction), three possible path ways were calculated regarding that three oxygen ($O_a/O_b/O_c$) in carbonate may interact with the OH group of phenol (Figure 6). For the α route, the interaction in **V**- α between 2-iodobutyl carbonate through O_a and O_c with OH of phenol is less favorable than that through O_b by 21 and 8 kJ·mol⁻¹, respectively. This indicates the strong stabilization of the carboxylate anion through the hydrogen bonding between the OH-group of the phenol and O_b and O_c of the carboxylate moiety, respectively.



Figure 6. The three possibilities of the stabilized intermediates $V\alpha(O_a, O_b and O_c)$ and the transition states $TS3-\alpha(O_a, O_b and O_c)$ in the C_α pathway. The structures of O_b hydrogen bonding interaction have the lowest energy.

For the last step through the groute, the ring closure through the O_a , O_b and O_c routes from the most stable V- α (O_b) via **TS3-\alpha** to the carbonate-catalyst adduct VI has an energy barrier of 91, 63 and 68 kJ·mol⁻¹, respectively. Notably, the formation of adduct V is exergonic by 60 kJ·mol⁻¹. For the β route, the interaction in V- β between 2-iodobutyl carbonate through O_b and O_c with OH of phenol is more favorable than that through O_a by 22 and 14 kJ·mol⁻¹, respectively. The ring closure through the O_{a} , O_{b} and O_{c} route from V- β (O_b) via TS3- β to form the adduct VI has an energy barrier of 78, 54 and 58 kJ·mol⁻¹, respectively. The formation of cyclic carbonate from V- β (O_b) is exergonic by 61 kJ·mol⁻¹. Notably, the release of the cyclic carbonate 2a from the catalystcarbonate adduct VI is exergonic by 14 kJ·mol⁻¹. This confirms the experimental finding that in the presence of catalyst 8 no product inhibition takes place. Overall, the Gibbs free energy profile shows that intermediate II is the resting state of the catalytic cycle. Interestingly, the ring-opening and ring-closing steps have very similar effective Gibbs energy barriers of 71 and 72 kJ \cdot mol⁻¹, respectively indicating that both steps can be rate-determining.

For catalyst 7, the Gibbs free energy profile (Figure S19) shows that the interaction of epoxide with phenol-derived phosphonium to form intermediate II- β_{Br} through the H-bond is endergonic by 27 kJ·mol⁻¹. The large energy difference indicates dynamic equilibrium in favor of I_{-Br} and 1a (>99.99 %) rather than $II_{-\beta_{Br}}$. For the ring-opening step, the β route is also more favorable than α route. The energy barrier of ring-opening via **TS1-\beta_{Br}** is 97 kJ·mol⁻¹ which is 5 kJ·mol⁻¹ lower than that via **TS1-\alpha_{Br}** It is worth noting that the formation of III- β_{Br} is highly exergonic by 22 kJ·mol⁻¹, while the formation of **III-\beta_1** is slightly endergonic by 6 $kJ \cdot mol^{-1}$. This indicates that the reaction with both, the Br⁻ catalyst 7 and \lceil catalyst 8, can compensate the increase of energy caused by ring-opening and the formation of 1-bromobutan-2-ol is more thermodynamically preferred. The following C-O coupling via **TS2-\beta_{Br}** has an energy barrier of 51 kJ·mol⁻¹. For the last step of ring-closing, the effective energy barrier via $TS3-\beta_{Br}(O_b)$ from **III-B**_{Br} is 86 kJ·mol⁻¹. In contrast to catalyst 8, the rate-determining step for the reaction in the presence of catalyst 7 is clearly the ring-opening. The effective barrier regarding this step for the bromide salt **7** is 97 kJ \cdot mol⁻¹, which is higher than that for iodide salt 8 (72 kJ·mol⁻¹) by 25 kJ·mol⁻¹. This can reasonably explain the superior catalytic activity of 8 compared to catalyst 7.

Conclusion

Bifunctional phenolic phosphonium salt catalysts showed superior efficiency in converting epoxides and CO₂ into value-added cyclic carbonates under mild and solvent-free conditions. The phenolbased phosphonium iodide **8** proved to be the most active catalyst. Notably, this catalyst showed high activity even at room temperature. Kinetic investigations revealed that the superior activity in comparison with the previously reported aliphatic catalyst **3** originates from a higher intrinsic activity as well as the absence of any product inhibition. In the model reaction the equilibrium constant K_{inh} of the product inhibition with the aliphatic catalyst was calculated as 0.260 L mol⁻¹. Moreover, the observable rate constants k^{ots} were determined as 0.197 h⁻¹ (**8**) > 0.0605 h⁻¹ (**3**) reflecting the catalytic activity. An apparent activation energy with a value of E_a =39.6 kJ·mol⁻¹ was estimated

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for the benchmark reaction with catalyst 8. The substrate scope was evaluated, and 20 terminal and 6 demanding internal epoxides were converted. Excellent results were achieved at room temperature for terminal epoxides while the conversion of internal epoxides required elevated reaction temperatures. Notably catalyst 8 showed high functional group to lerance and the desired cyclic carbonates were isolated in yields up to 99% even on multi gram scale (up to 50 g substrate). Furthermore, this method was applied in the three-step synthesis of antitussive agent dropropizine starting from epichlorohydrin and phenylpiperazine. On the basis of the experimental findings the full Gibbs free energy surface for the use of phenol-derived phosphonium halides 7 and 8 as catalysts in the model reaction were calculated. The calculation confirmed the activation of the epoxide via hydrogen bonding for the iodide salt which facilitates the ring-opening step. Notably, the effective barrier regarding this step is 97 kJ·mol⁻¹ for the bromide and 72 kJ·mol⁻¹ for the iodide salt which clearly explains the difference in activity. The DFT calculations also confirmed the experimental finding that no product inhibition occurs in the presence of the phenol-based phosphonium iodide. Interestingly, for catalyst 8 the ring-opening and ring-closing steps have similar effective Gibbs energy barriers of 71 and 72 kJ·mol⁻¹, respectively indicating that both steps can be rate-determining. In contrast for catalyst 7 the ratedetermining step is the epoxide opening with an effective Gibbs energy barrier of 97 kJ \cdot mol⁻¹.

Experimental Section

Synthesis of catalyst 8

2-(Diphenylphosphanyl)phenol:^[52] Under argon a mixture of 2-iodophenol (660 mg, 3.00 mmol, 1.00 equiv), Pd(OAc)₂ (6.7 mg, 0.029 mmol, 0.03 equiv), NaOAc (271 mg, 3.30 mmol, 1.10 equiv) was dissolved in anhydrous DMA (9.00 mL). After addition of diphenylphosphine (559 mg, 3.00 mmol, 1.00 equiv) the reaction mixture was heated to 110 °C and stirred for 17 h. Subsequently, the reaction mixture was cooled to 23 °C and filtered over celite using CH₂Cl₂ as eluent. After removal of all volatiles in vacuo the crude product was purified by column chromatography (SiO₂, CH₂Cl₂) to yield the title compound (710 mg, 2.55 mmol, 83%) as a colorless solid. ¹H NMR (300 MHz, CDCl₃, 25 °C): \doteq 6.26–6.28 (br s, 1H), 6.88–7.03 (m, 3H), 7.29–7.39 (m, 11H) ppm. ³¹P NMR (122 MHz, CDCl₃, 25 °C): \bigstar -28.62 ppm.

(2-Hydroxyphenyl)diphenyl(propyl)phosphonium iodide (8):^[32] In a pressure tube 1-iodopropane (2.17 g, 12.8 mmol) was added to 2-(diphenylphosphanyl)phenol (510 mg, 2.55 mmol). The tube was flushed with argon and sealed. Subsequently, the reaction mixture was stirred at 102 °C for 24 h. The crude product was filtered off and washed with Et₂O (4x50 mL) to yield **8** (1.06 g, 2.37 mmol, 93%) as a white solid. ¹H NMR (300 MHz, CDCl₃): & 1.14 (td, *J*= 7.3, 1.9 Hz, 3H), 1.68–1.81(m, 2H), 3.08–3.18 (m, 2H), 6.84–6.92 (m, 1H), 6.94–7.01 (m, 1H), 7.53–7.69 (m, 9H), 7.75–7.82 (m, 2H), 7.96–8.01 (m, 1H), 10.78 (br s, 1H) ppm. ³¹P NMR (122 MHz, CDCl₃) & 23.49 ppm.

Representative examples for the synthesis of cyclic carbonates

4-Methyl-1,3-dioxalan-2-one (2a):^[53] A 45 cm³ stainless-steel autoclave was charged with catalyst 8 (306 mg, 0.683 mmol, 5 mol%) and 1,2-epoxybutane (1a, 1.00 g, 13.9 mmol). The autoclave was purged with CO₂. Subsequently, the reaction mixture was stirred at 23 °C for 24 while $p(CO_2)$ was kept constant at 1.00 MPa. CO₂ was released slowly, and the reaction mixture was filtered over silica (SiO₂) with EtOAc as eluent. After the

removal of all volatiles in vacuo **2a** (1.53 g, 13.1 mmol, 95%) was obtained as a light yellow oil. ¹H NMR (300 MHz, CDCI₃) \succeq 1.03 (t, *J*= 7.4 Hz, 3H), 1.66–1.93 (m, 2H), 4.09 (dd, *J*= 8.4, 7.0 Hz, 1H), 4.53 (dd, *J*= 8.4, 7.9 Hz, 1H), 4.61–4.74 (m, 1H) ppm.

4-(Methoxymethyl)-1,3-dioxalan-2-one (**12a**):^[53] A 45 cm³ stainless-steel autoclave was charged with 2-(methoxymethyl)oxirane (**11a**, 1.00 g, 11.4 mmol) and catalyst **8** (254 mg, 0.567 mmol, 5 mol%). The autoclave was purged with CO₂. Subsequently, the reaction mixture was stirred at 23 °C for 48 h while $p(CO_2)$ was kept constant at 1.00 MPa. CO₂ was released slowly, and the reaction mixture was filtered over silica (SiO₂) with EtOAc as eluent. After the removal of all volatiles in vacuo **12a** (1.44 g, 10.9 mmol, 96%) was obtained as a yellow liquid. ¹H NMR (300 MHz, CDCl₃) & 3.43 (s, 3H), 3.58 (dd, *J*= 10.9, 3.8 Hz, 1H), 3.63 (dd, *J*= 3.9 Hz, 1H), 4.39 (dd, *J*= 8.4, 6.1 Hz, 1H), 4.50 (t, *J*= 8.3 Hz, 1H), 4.75–4.87 (m, 1H) ppm.

cis-Tetrahydrofuro[3,4-d][1,3]dioxol-2-one (14c):^[53] A 45 cm³ stainlesssteel autoclave was charged with 6-dioxabicyclo[3.1.0]hexane (13c, 1.00 g, 11.6 mmol) and catalyst 8 (261 mg, 0.582 mmol, 5 mol%). The autoclave was purged with CO₂. Subsequently the mixture was stirred at 80 °C for 24 h, while *p*(CO₂) was kept constant at 2.50 MPa. The reactor was cooled with an ice bath below 20 °C and CO₂ was released slowly. The reaction mixture was filtered over silica gel (SiO₂) with EtOAc as eluent. After the removal of all volatiles in vacuo the desired products 14c (1.25 g, 9.61 mmol, 82%) was obtained as a colorless liquid.

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Keywords: CO₂ fixation • Organocatalysts • Homogeneous Catalysis • Cyclic carbonates • Mechanism

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- [51] CCDC 2024624 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.
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Phen of functionalized phosphonium salts are efficient catalysts for the synthesis of cyclic carbonates under mild and solvent-free conditions. Their superior activity was elucidated by kinetic investigations and DFT calculations.