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Advancements in six-membered cyclic carbonate (1,3-dioxan-2-one) synthesis utilizing carbon dioxide as a C1 source

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This review article surveys literature methods for the synthesis of six-membered cyclic carbonates using various substrates in the presence of CO₂ with special emphasis on the mechanistic aspects of the reactions. We have classified these reactions based on the type of starting material.

1. Introduction

Needless to say that the global warming trend and climate change are caused by the emission of greenhouse gases into the Earth's atmosphere. Interestingly, ~72% of the total emitted greenhouse gases is carbon dioxide (CO₂) and every year, human activity releases ~38 000 million tons of this gas into the atmosphere.¹ Growing environmental concerns in recent years for global warming, climate change, and ocean acidification have motivated research activities toward developing efficient

and green strategies to capture, store, and utilize CO₂.^{1,2} On the other hand, from the viewpoint of chemistry, CO₂ is considered as an abundant, inexpensive, nontoxic, nonflammable, and renewable carbon feedstock for producing value-added organic compounds (e.g. alcohols, carboxylic acids, esters, aldehydes, amides, urethanes, ureas, quinazoline-2,4(1*H*,3*H*)-diones, and carbonates).^{3–13} However, most reactions involving CO₂ require the use of stoichiometric amounts of catalysts and/or drastic reaction conditions.^{14,15} Therefore, development of more-efficient and improved synthetic protocols for chemical transformation of CO₂ is a very attractive topic in modern organic synthesis.

1,3-Dioxan-2-one is a cyclic carbonate ester having the chemical formula C₄H₆O₃. This potential monomer continues to play an overwhelming role in the synthesis of aliphatic polycarbonates and polyurethanes, which are of interest for

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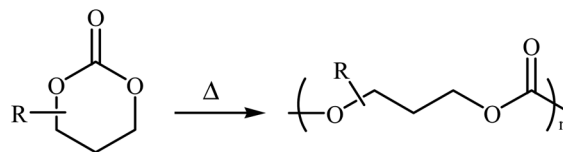


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biomedical applications because of their low toxicity and biodegradability.^{16–19} The most common preparation of 1,3-dioxan-2-one (six-membered cyclic carbonate) monomers involves the reaction of 1,3-diols with phosgene derivatives^{20,21} or carbon monoxide.²² However, both phosgene and CO are very toxic, which extremely limits their employment in academic and industrial research. Over the past few years, CO₂ has emerged as an alternative to phosgene and CO in carbonate synthesis.^{23,24} Along this line, various synthetic organic chemists have put forward considerable efforts in the synthesis of five- and six-membered cyclic carbonates using various substrates in the presence of CO₂. Due to the inherent thermodynamic instability of six-membered cyclic carbonates (Scheme 1), synthesis of these compounds utilizing CO₂ as a C1 source is much less studied than the corresponding five-membered cycles.

As a part of our continual review papers on the chemical conversion of CO₂ into value-added organic compound,^{15,26} herein we will highlight the most important advances on the



Scheme 1 The ring-opening polymerization of 1,3-dioxan-2-ones is thermodynamically favored at all temperatures.²⁵

synthesis of six-membered cyclic carbonates using various substrates in the presence of CO₂ (Fig. 1), by hoping that it will stimulate researchers to develop more-efficient and improved methods for the synthesis of these extremely important potential monomers with sustainable and green chemistry perspectives. It should be mentioned that special emphasis is laid on mechanistic aspects of the reactions.

2. From 1,3-diols

Chemical fixation of carbon dioxide to 1,2-diols is a well-known synthetic route to five-membered cyclic carbonates and has been the subject of numerous research studies and reviews.²⁷ In contrary, direct six-membered cyclic carbonates synthesis from carbon dioxide and 1,3-diols has been seldom addressed in the literature. One of the earliest general methods for six-membered cyclic carbonates synthesis through carboxylative cyclization of 1,3-diols with CO₂ was published in 2014, by Honda *et al.*²⁸ They showed that treatment of diols **1** with CeO₂ as a catalyst and 2-cyanopyridine as a dehydrating agent under the CO₂ atmosphere (5 MPa) furnished corresponding six-membered cyclic carbonates **2** in good to excellent yields (Scheme 2). It is noted that the presence of 2-cyanopyridine was crucial to the success of this reaction. In the absence of 2-cyanopyridine very low yield of desired product was observed, which is due to the equilibrium limitation. The mechanistic pathway by the authors for this cyclization starts with the formation of cerium alkoxide species **A** from the adsorption of



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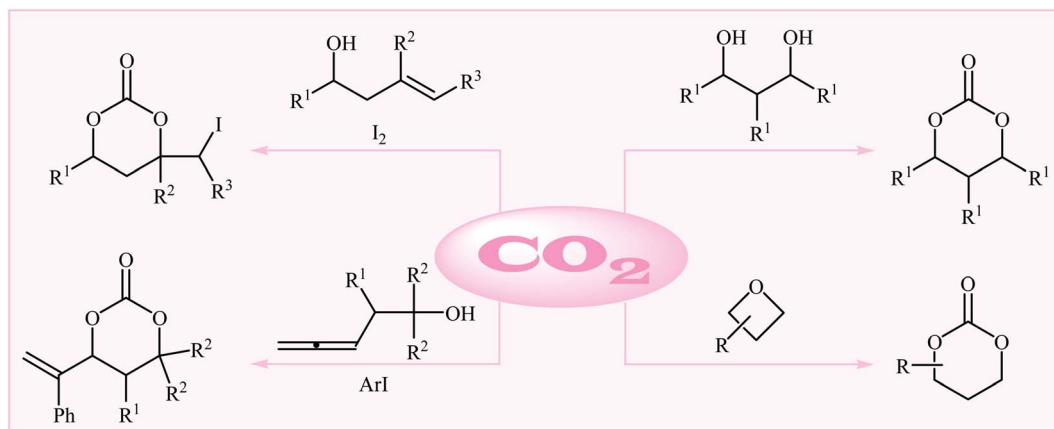
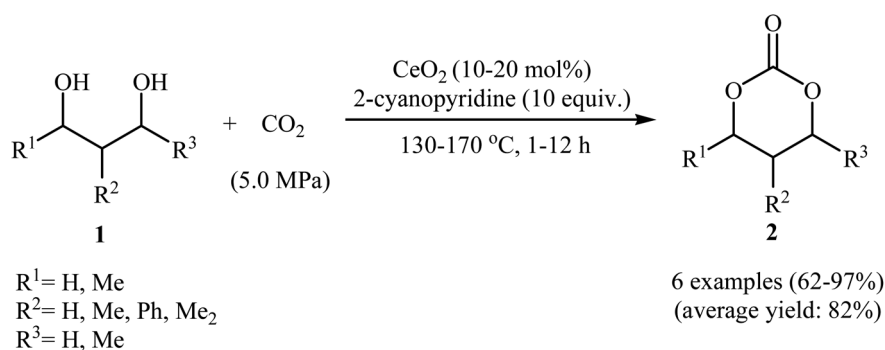
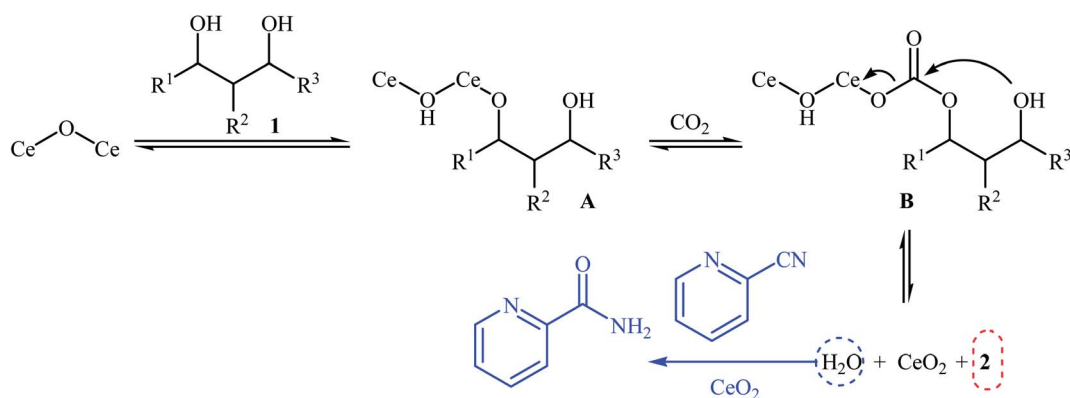


Fig. 1 Synthesis of six-membered cyclic carbonates using various substrates in the presence of CO_2 .



Scheme 2 CeO_2 -catalyzed synthesis of six-membered cyclic carbonates **2** from 1,3-diols **1** and CO_2 developed by Honda *et al.*²⁸



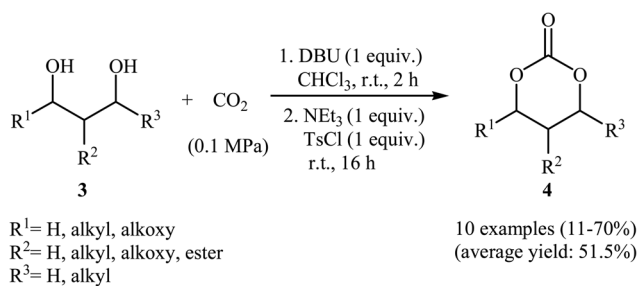
Scheme 3 Mechanism that accounts for the formation of carbonates **2**.

one OH group of diol **1** to Lewis acid sites of CeO_2 , followed by insertion of CO_2 into the Ce–O bond in intermediate **A** to give alkyl carbonate species **B**. Next, intramolecular nucleophile attack of the other OH group to the carbonyl carbon in intermediate **B** leads to the cyclic carbonate **2** and one molecule of water with concomitant regeneration of CeO_2 . Finally, hydration of 2-cyanopyridine with the produced water affords corresponding amide (Scheme 3).

Subsequently, with the objective of designing a milder procedure to six-membered cyclic carbonates *via* the

carboxylative cyclization of 1,3-diols with CO_2 , Gregory, Ulmann and Buchard were able to demonstrate that a series of substituted carbonates **4** could be obtained in satisfactory yields from the reaction of corresponding diols **3** with CO_2 under very mild conditions (room temperature and atmospheric pressure) employing 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) as a promotor and CHCl_3 as the solvent (Scheme 4). Important functional groups such as ester and ether functionalities that would allow further elaboration of the products were well tolerated under this reaction conditions. The authors investigated the





Scheme 4 Buchard's synthesis of six-membered cyclic carbonates 4.

detailed reaction mechanism with density functional theory (DFT) calculations. As shown in Fig. 2 this reaction proceeds through an addition/elimination pathway.²⁹

Very recently, the same research team prepared a novel D-mannose-based cyclic carbonate 6 from natural sugar D-mannose 5 and CO₂ using their standard reaction conditions and successfully applied this monomer in the synthesis of polycarbonates 7 via a controlled organocatalytic ring-opening polymerization (Scheme 5).^{30,31}

In 2016, Bobbink and co-workers reported an innovative example of six-membered cyclic carbonate 9 preparation

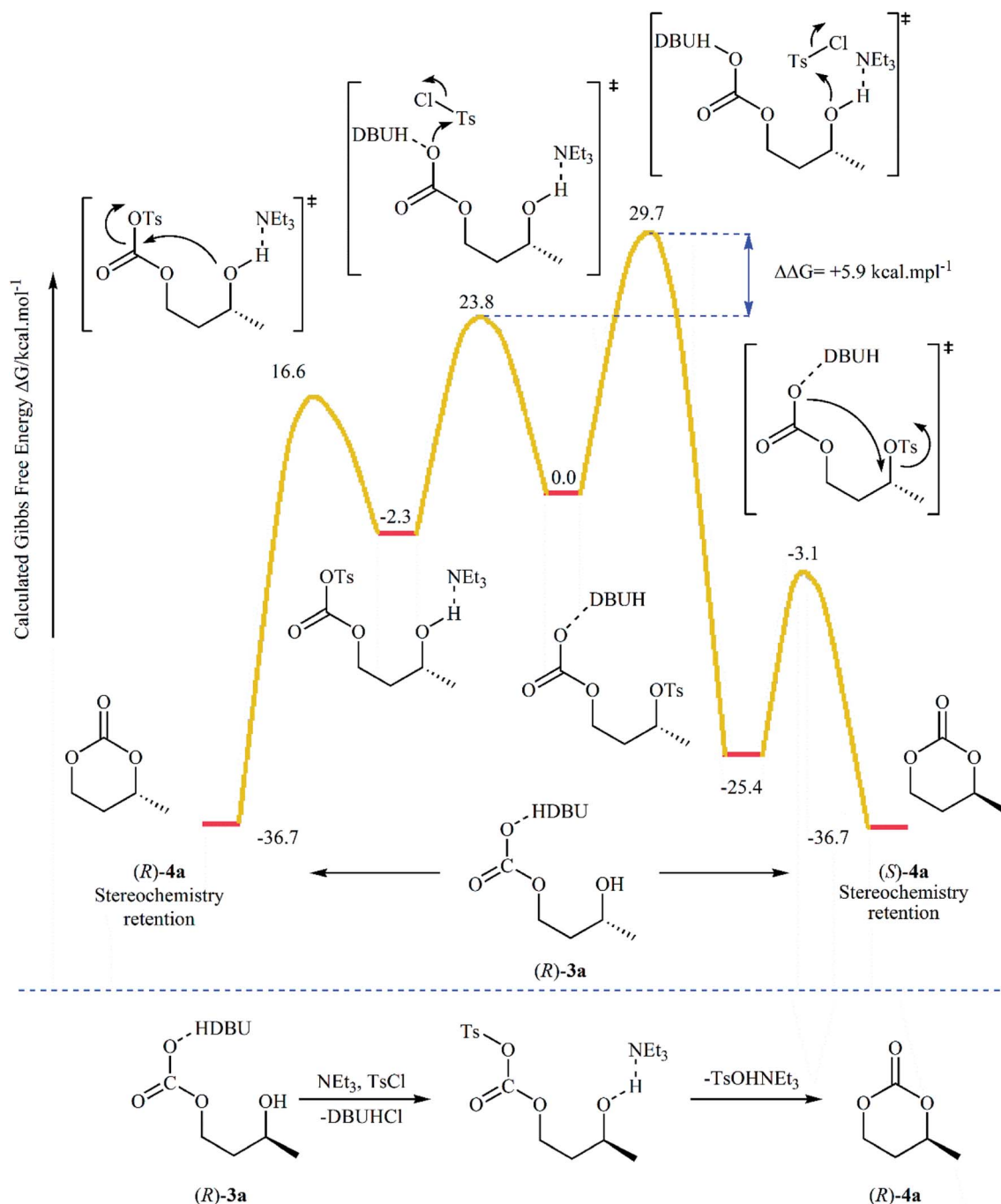
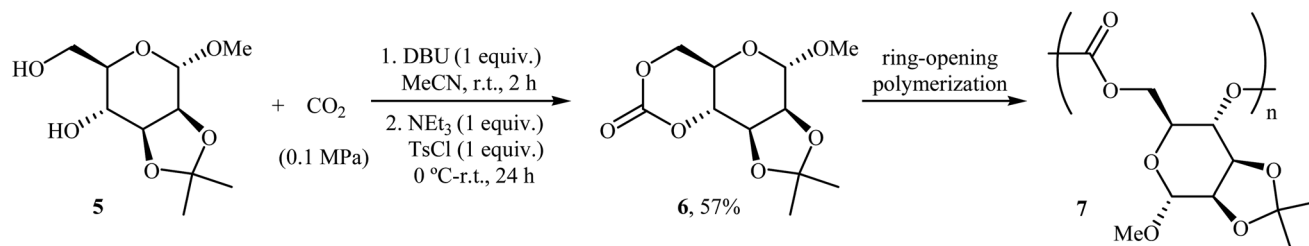
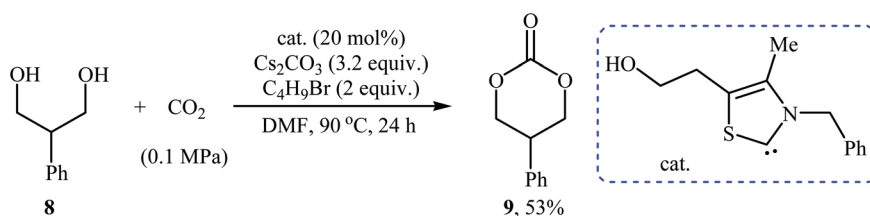


Fig. 2 DFT computed pathways and mechanism for the cyclization of 3a to 4a.

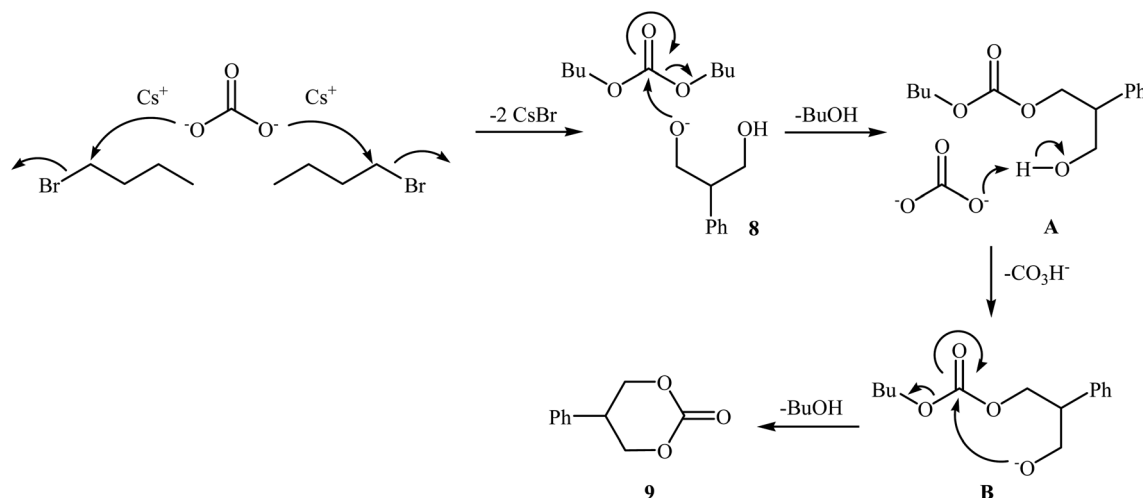




Scheme 5 Synthesis and polymerization of a D-mannose-based cyclic carbonate 6.



Scheme 6 Synthesis of six-membered cyclic carbonate 2 through carbene-catalyzed fixation of CO₂ onto 1,3-diols 8.



Scheme 7 Mechanistic proposal for the reaction in Scheme 6.

through a carbene-catalyzed fixation of CO₂ onto corresponding 1,3-diol **8**. The reaction was performed at the atmospheric pressure of CO₂ in the presence of over stoichiometric amounts of ^tBuBr and Cs₂CO₃ to produce expected carbonate **2** in yield of 51% (Scheme 6). It is noted that both the base and alkyl halide are essential in the reaction, no carbonate was formed in their absence. Based on labeling studies and other experiments the mechanism shown in Scheme 7 was proposed for this reaction.³²

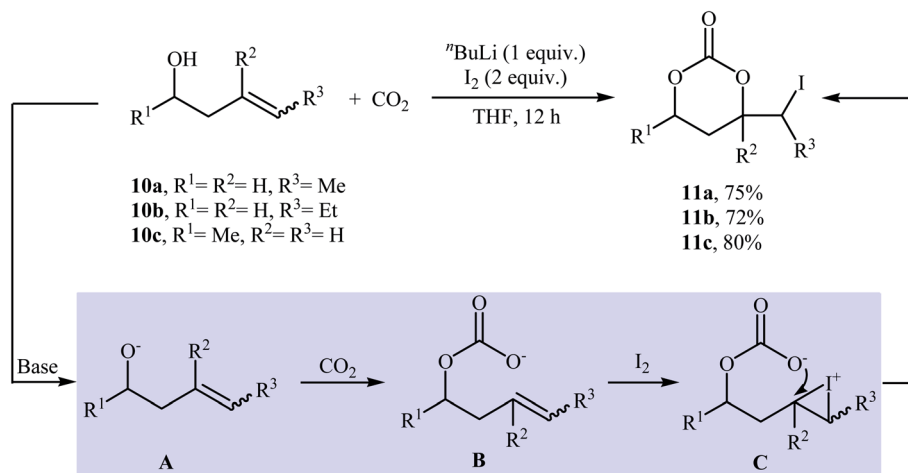
3. From homoallylic alcohols

In 1981, in a beautiful approach, Cardillo and co-workers disclosed a one-pot, three-component reaction between homoallylic alcohols **10**, carbon dioxide, and molecular iodine for the regio- and stereo-selective synthesis of six-membered cyclic

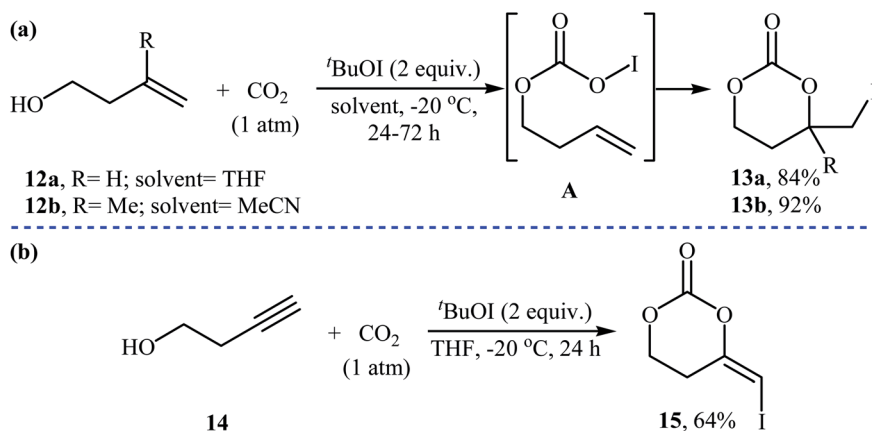
carbonates **11** using ^tBuLi as a base in dry THF (Scheme 8). The authors suggested that the formation of **11** occurs *via* addition of CO₂ to the alkoxide group in intermediate **A**, followed by a formal electrophilic iodocyclization sequence. They also successfully extended this chemistry to synthesis of five-membered cyclic carbonates *via* the reaction of corresponding allylic alcohols with CO₂ and I₂ under standard conditions.³³

Three decades later, an interesting study about metal-free and base-free atmospheric CO₂ fixation by homoallylic alcohols **12** using *tert*-butyl hypoiodite (^tBuOI) as a reactive iodonium source, was published by Minakata, Sasaki, and Ide. The reactions proceeded cleanly at −20 °C in THF (or MeCN) to afford the corresponding iodinated six-membered cyclic carbonates **13** in high yields (Scheme 9a). According to the author proposed mechanism, the key step of the reaction involve generation of an O-iodinated intermediate **A** by





Scheme 8 Base-mediated three-component reactions of homoallylic alcohols **10**, CO_2 , and I_2 developed by Cardillo.



Scheme 9 (a) Atmospheric CO_2 fixation with homoallylic alcohols **12** and $t\text{BuOI}$ reported by Minakata; (b) CO_2 fixation with butynyl alcohol **14** and $t\text{BuOI}$.

iodination of the *in situ* generated homoallyl carbonic acid with $t\text{BuOI}$. They also found that butynyl alcohol **14** was converted to the corresponding six-membered cyclic carbonate **15**, *via* treatment with $t\text{BuOI}$ under the CO_2 atmosphere at -20°C (Scheme 9b). To the best of our knowledge, this is the only example of synthesis of cyclic carbonates from butynyl alcohols reported so far.³⁴

Inspired by these works, Johnston and co-workers developed a beautiful one-pot procedure for the enantioselective synthesis of six-membered cyclic carbonates *via* a dual Brønsted acid/base organocatalyzed three component reaction between homoallylic alcohols, carbon dioxide, and *N*-iodosuccinimide. Under the optimized conditions [StilbPBAM **16** (5 mol%), HNTf₂ (5 mol%), NIS (1.1 equiv.) toluene, -20°C , 0.1 MPa] various homoallylic alcohols **17** react to give moderate to excellent yields of the corresponding carbonates **18** in high enantioselectivity (Table 1). The reaction showed good functional group diversity, including fluoro, chloro, bromo, and alkoxy functionalities that would allow further elaboration of the products to structurally diverse carbonates. However, substitution near the alkene moiety was not tolerated and no desired product was

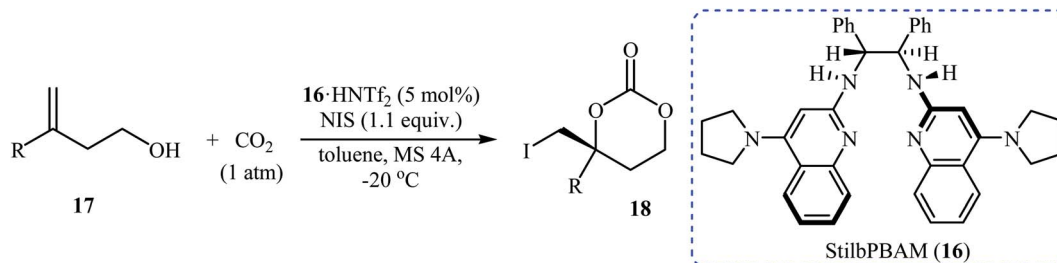
obtained in these cases. The authors investigated the synthetic utility of prepared carbonates (Scheme 10a) and found that hydrolysis of **18a** with a basic resin in methanol provided the corresponding epoxide **19** in a yield of 90%. Full reduction employing a stronger reducing agent (LiAlH_4) gave tertiary alcohol **20** in a yield of 71% and reduction by stannane provided carbonate **21** in 86% yield. They also showed that carboxylation/alkene functionalization reaction of 2-cyclohexenylethanol **22** under the standard reaction conditions provided a useful route to enantio-rich spirocyclic carbonate **23** (Scheme 10b).³⁵

4. From oxetanes

The synthesis of five-membered cyclic carbonates through the ring-expansion of oxiranes with CO_2 is a well-established reaction,³⁶ whereas the synthesis of six-membered cyclic carbonates from oxetanes and CO_2 is considerably more challenging,³⁷ and few efficient catalysts are available. In 1985, Baba, Kashiwagi and Matsuda reported the first example of such a reactions. They showed that unsubstituted oxetane **24** underwent ring-expansion with CO_2 (4.9 MPa) in the presence of 2 mol% of

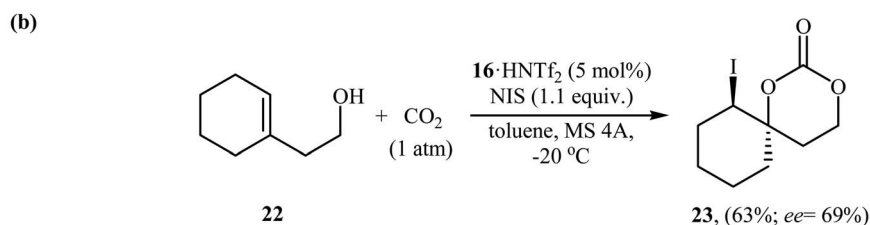
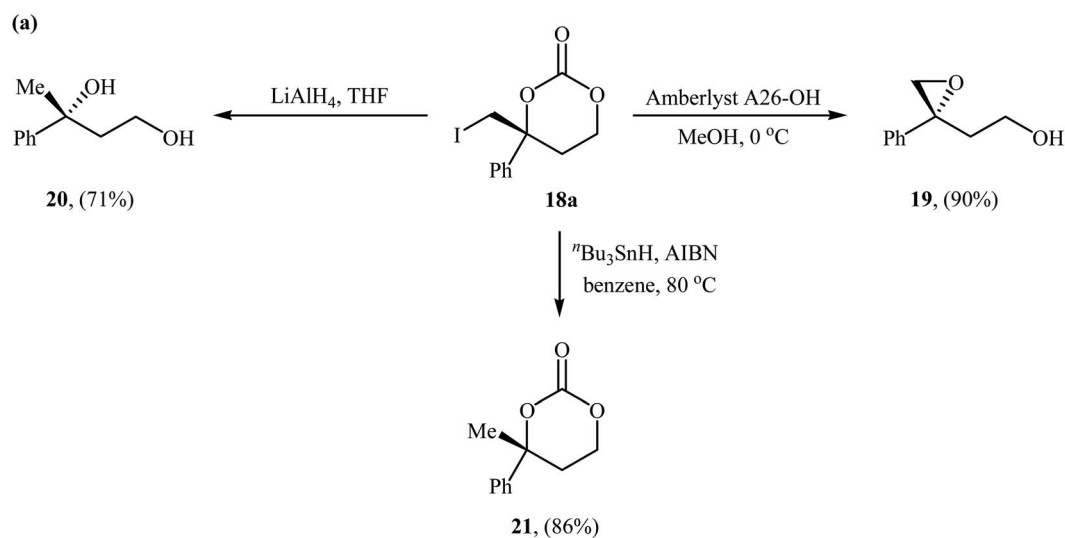


Table 1 Enantioselective synthesis of six-membered cyclic carbonates **18** via a dual Brønsted acid/base organocatalyzed three component reaction between homoallylic alcohols **17**, CO₂, and *N*-iodosuccinimide



Entry	R	Product	Time (h)	ee (%)	Yield (%)
1	Ph	18a	48	91	95
2	4-Me-C ₆ H ₄	18b	48	91	96
3	3-Me-C ₆ H ₄	18c	48	93	96
4	2-Naphthyl	18d	48	90	88
5	4-OMe-C ₆ H ₄	18e	48	80	26 ^a
6	3-OMe-C ₆ H ₄	18f	48	90	97
7	4-Br-C ₆ H ₄	18g	48	90	65
8 ^b	3-Cl-C ₆ H ₄	18h	120	87	44
9 ^b	3-F-C ₆ H ₄	18i	96	89	40
10	4-F-C ₆ H ₄	18j	48	90	54
11	4-(Me ₃ C)-C ₆ H ₄	18k	48	91	99
12	PhCH ₂ CH ₂	18l	72	67	71
13	Me	18m	48	68	72
14 ^b	Cy	18n	48	74	76

^a It was noted that purified **18e** was prone to decomposition. ^b 10 mol% catalyst loading.

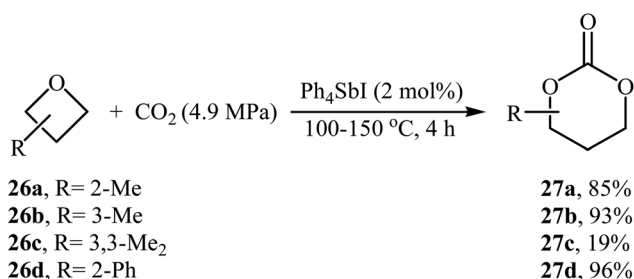
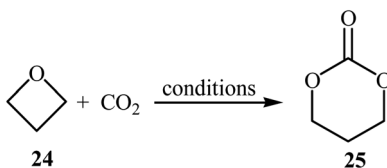


Scheme 10 (a) Conversions of carbonate **18a** to various value-added organic compounds; (b) Vara's synthesis of spirocyclic carbonate **23**.



Table 2 Ring-expansion of oxetane **24** with CO₂

Entry	Conditions	Yield (%)	Ref.
1	Ph ₄ SbI (2 mol%), 4.9 MPa, 100 °C, 4 h	96	38
2	Bu ₃ SnI (2 mol%), HMPA (20 mol%), 4.9 MPa, 100 °C, 24 h	100	39
3	VO(acac) ₂ (5 mol%), <i>n</i> -Bu ₄ NBr (5 mol%), toluene, 3.5 MPa, 60 °C, 8 h	95	40

Scheme 11 Ph₄SbI-catalyzed coupling of oxetanes **26** and CO₂.

Ph₄SbI as a catalyst under solvent-free conditions and gave corresponding carbonate **25** in a yield of 96% (Table 2, entry 1). The authors found that the yield in this system was strongly dependent on the temperature. The best results were obtained at 100 °C. It is interesting to note that neither Ph₃SbI₂ nor Ph₄SbBr could promote the reaction under the similar conditions.³⁹ Two years later, the same authors improved the efficiency of this cycloaddition in the term of yield by performing the reaction in the presence of a combination of Bu₃SnI and HMPA as a catalytic system and obtained desired carbonate in a quantitative yield (Table 2, entry 2).³⁹ Later, the group of Darensbourg showed that heating of the same starting materials at 60 °C in the presence of VO(acac)₂/*n*-Bu₄NBr system in toluene gave expected carbonate **25** in a yield of 95% (Table 2, entry 3).⁴⁰

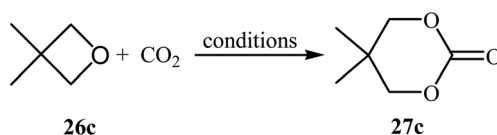
In 1989, the group of Baba applied their methodology to the synthesis of substituted six-membered cyclic carbonates. Thus,

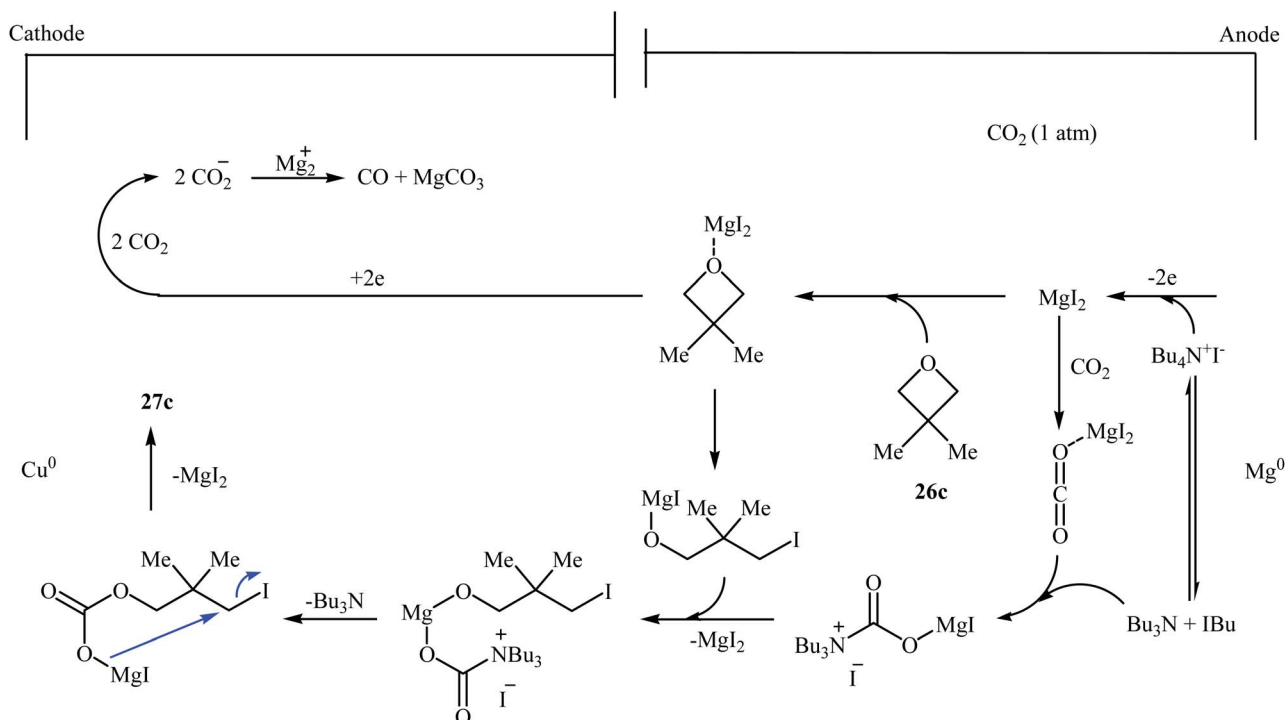
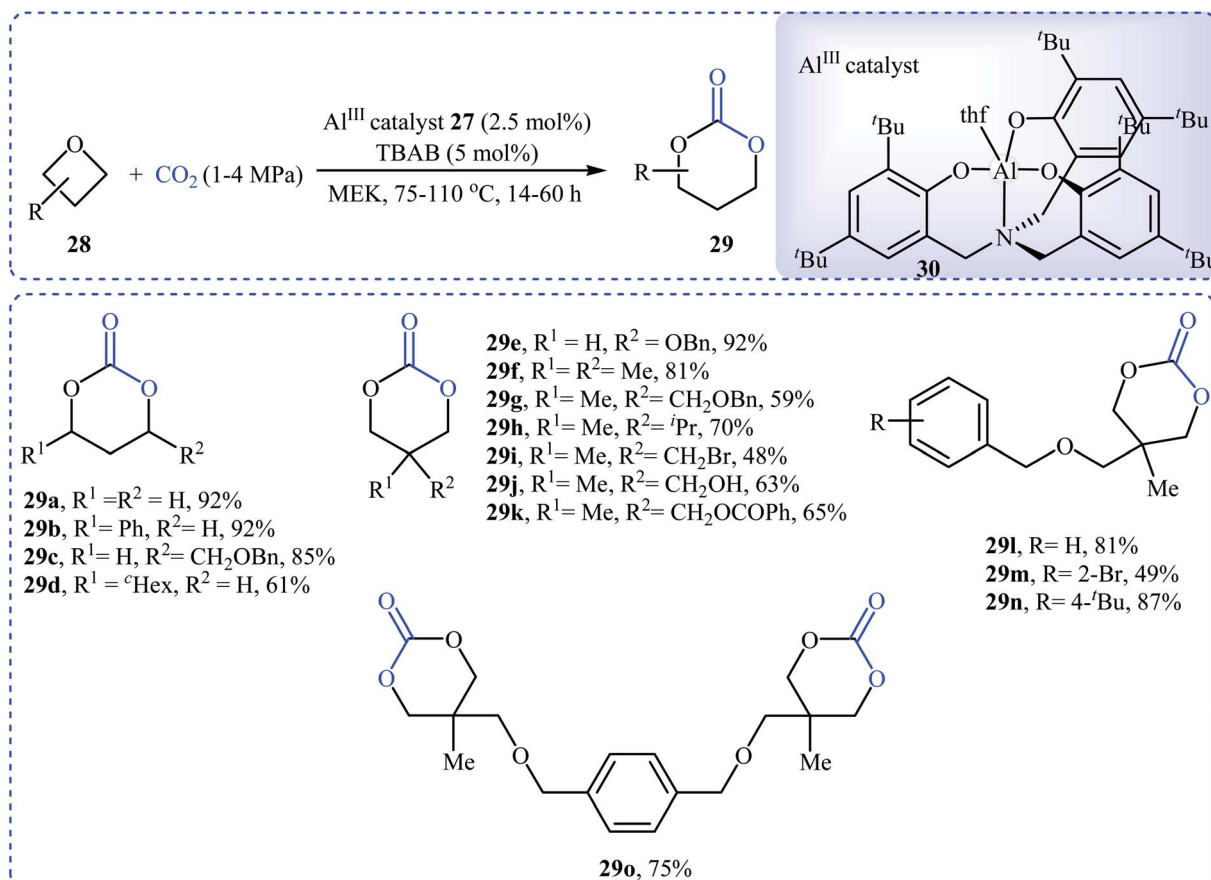
a series of mono- and di-substituted carbonates **27** were synthesized *via* the Ph₄SbI-catalyzed reaction of corresponding oxetanes **26** and CO₂ under solvent-free conditions (Scheme 11). The results demonstrated that mono-substituted oxetanes gave much higher yields than di-substituted oxetanes under this reaction conditions. The reaction is noteworthy in that both alkyl and aryl substituted oxetanes are well tolerated.⁴¹

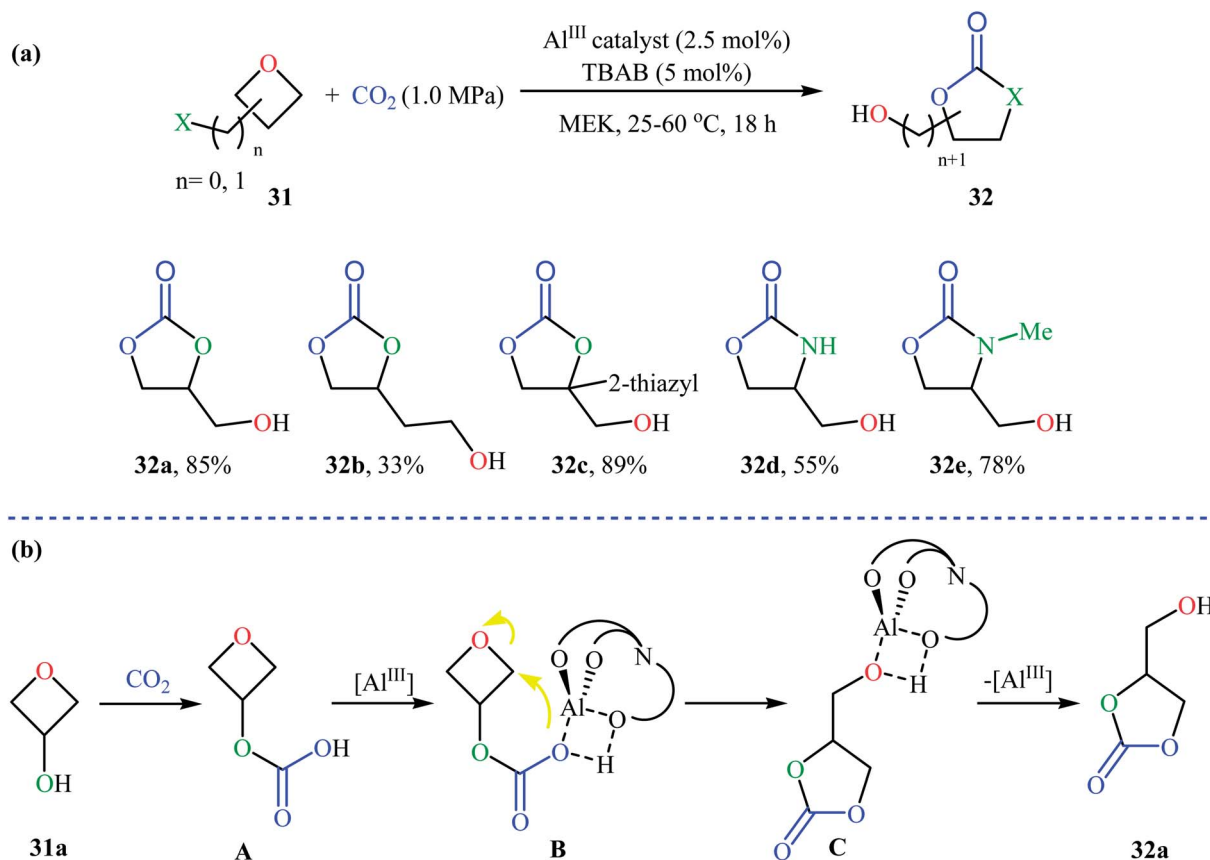
Following this work, several catalytic systems have been developed over the last several years towards the improvement of the yields of di-substituted six-membered cyclic carbonates under this synthetic protocol. In 2012, the group of Kleij reported the preparation of 5,5-dimethyl-1,3-dioxan-2-one **27c** *via* ring-expansion of 3,3-dimethyloxetane **26c** with CO₂ using only 0.5 mol% of [Fe(TPhOA)]₂ as a catalyst and 5 mol% of Bu₄NI as a co-catalyst in methyl ethyl ketone at 85 °C. The reaction was carried out under 0.2 MPa pressure of CO₂ to afford within 66 h the corresponding carbonate in 28% yield (Table 3, entry 1).⁴² In their subsequent study, they reinvestigated the same reaction by replacing [Fe(TPhOA)]₂ with an Al triphenolate catalyst. However, the process resulted in a reduced yield (Table 3, entry 2).⁴³ In 2015, Buckley, Patel, and Wijayantha were able to improve this reaction with a considerable increase in yield by performing the process under electrosynthesis conditions using an electrochemical cell containing a copper cathode and a magnesium anode and 1.0 equiv. of Bu₄NI as a supporting electrolyte in MeCN (Table 3, entry 3).⁴⁴ High yield and mild reaction condition (50 °C, 0.1 MPa) were the advantages mentioned for this catalyst-free synthetic approach. The author proposed mechanism for this reaction is shown in Scheme 12.

Table 3 Fixation of CO₂ with 3,3-dimethyloxetane **26c**

Entry	Conditions	Yield (%)	Ref.
1	[Fe(TPhOA)] ₂ (0.5 mol%), Bu ₄ NI (5 mol%), Me-CO-Et, 0.2 MPa, 85 °C, 66 h	28	42
2	Al triphenolate catalyst (0.5 mol%), Bu ₄ NI (2.5 mol%), 1 MPa, 70 °C, 18 h	26	43
3	Cu cathode, Mg anode, Bu ₄ NI (1 equiv.), MeCN, 0.1 MPa, 50 °C, 6 h	70	44



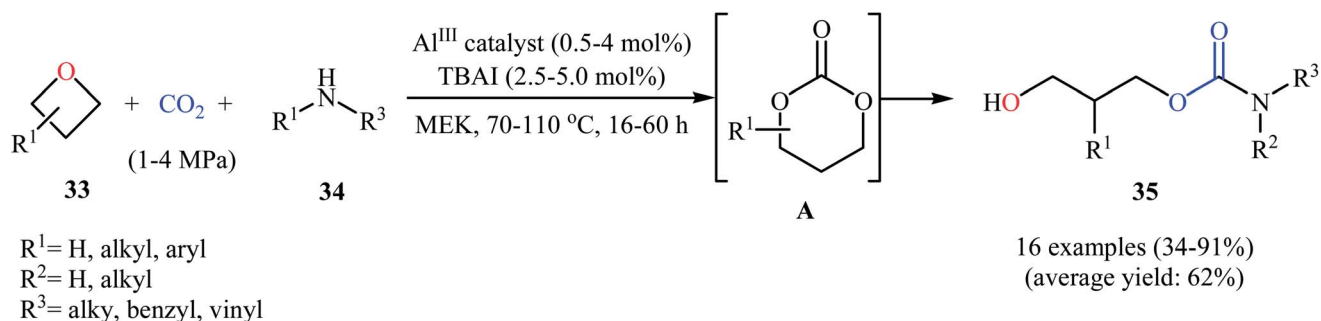
Scheme 12 Proposed mechanism for the formation of **27c** under electrosynthesis conditions.Scheme 13 Al^{III} -catalyzed coupling of oxetanes **28** with CO_2 reported by Kleij.



Scheme 14 (a) Synthesis of five-membered heterocycles **32** through Al(III)-catalyzed coupling of amino- and hydroxy-substituted oxetanes **31** with CO₂; (b) mechanism proposed to explain the synthesis of **32**.

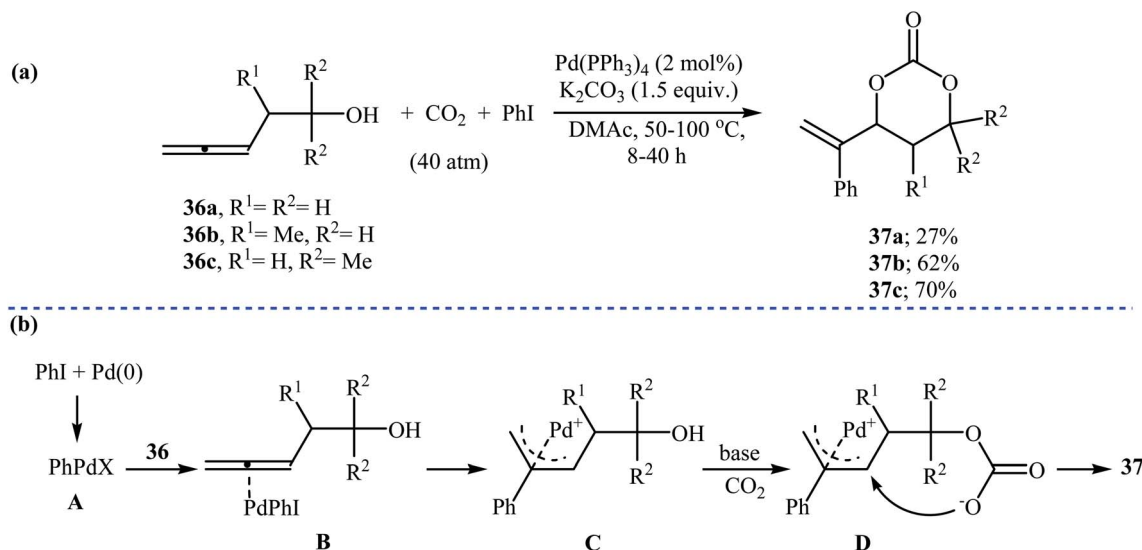
Recently, Kleij's group presented one of the most striking examples of the synthesis of substituted six-membered cyclic carbonates **29** *via* an Al(III)-catalyzed coupling of corresponding oxetanes **28** with carbon dioxide (Scheme 13). Under the optimized conditions (Al^{III}-aminotriphenolate complex **30**, tetrabutylammonium bromide (TBAB), methyl ethyl ketone, 1–4 MPa, 75 °C) various 2-, 3-, and 3,3-disubstituted oxetanes react to give moderate to almost quantitative yields of the corresponding carbonates. The reaction tolerated a variety of sensitive functional groups, including bromo, hydroxy, alkoxy, and ester functionalities that would allow further elaboration of the products. Interestingly, when similar reaction conditions were

applied to the oxetane precursors having pendent hydroxyl or amino substituents **31**, the formation of five-membered heterocycles **32** were obtained in moderate to high yields, without any of expected six-membered cyclic carbonates (Scheme 14a). According to the author proposed mechanism this reaction proceeds *via* the initial formation of carbamic or carbanic acid derivative **A** from the starting oxetane **31** and CO₂. Next, coordination of the catalyst to the intermediate **A**, leading to the formation of complex **B**, which then undergoes an intramolecular S_N2 reaction to produce intermediate **C**. Finally, reductive elimination of aluminum affords the observed carbonates/carbamates **32** (Scheme 14b).⁴⁵



Scheme 15 Al(III)-catalyzed synthesis of acyclic carbamates **35** from the reaction between oxetanes **33**, amines **34**, and CO₂.



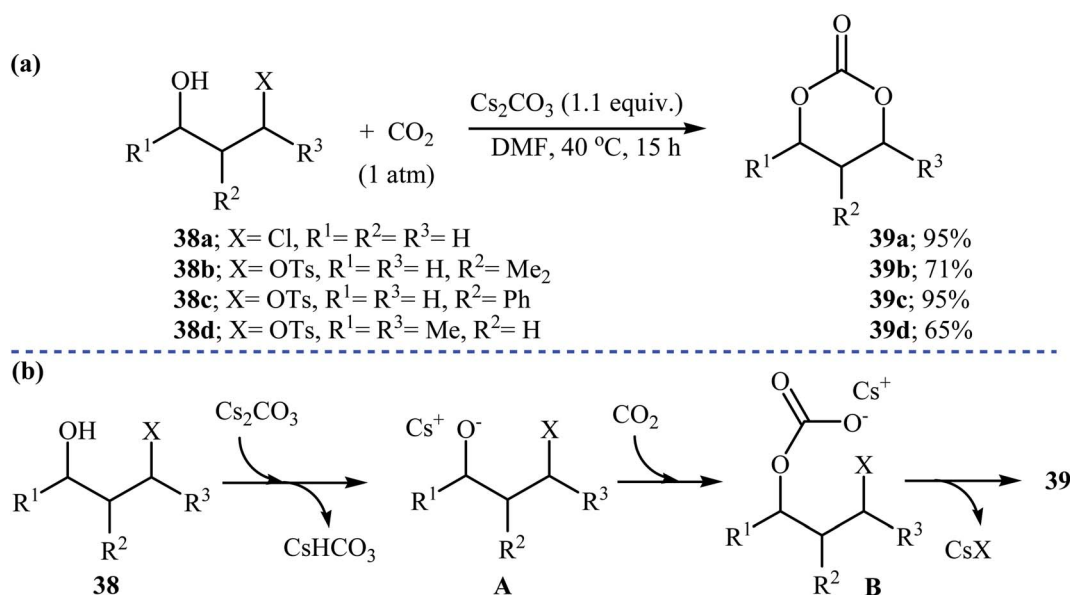


Scheme 16 (a) synthesis of highly substituted six-membered cyclic carbonates **37** via a Pd-catalyzed three-component reaction of 3,4-alkadienols **36**, phenyl iodide, and CO_2 ; (b) mechanism that accounts for the formation of **37**.

Very recently, the same research team extended this methodology to the high yielding synthesis of highly functionalized acyclic carbamates **35** *via* a one-pot three-component coupling between oxetanes **33**, amines **34**, and CO_2 under their optimized conditions (Scheme 15). According to mechanistic studies, it proceeds through the formation of a six-membered cyclic carbonate from the starting oxetanes and CO_2 , followed by an *in situ* aminolysis of these carbonates. It should be mentioned that the authors successfully showed the application of this methodology for the high yielding synthesis of carisoprodol, a muscle relaxer drug, and the mono-carbamate of Felbatol, an anticonvulsant drug.⁴⁶

5. Miscellaneous reactions

In 1999, Uemura and co-workers developed an efficient palladium catalyzed three-component reaction of 3,4-alkadienols **36**, phenyl iodide, and CO_2 , which allowed for the synthesis of highly substituted six-membered cyclic carbonates **37** in moderate yields (Scheme 16a). The authors also successfully applied this methodology in the synthesis of a variety of five-membered cyclic carbonates *via* the coupling of 3,4-alkadienols with aryl/vinyl halides and CO_2 . According to the author proposed mechanism, this reaction starts with the formation of phenylpalladium(II) species **A** *via* oxidative addition of phenyl



Scheme 17 (a) Synthesis of six-membered cyclic carbonates **39** from 3-(pseudo)halo-1-propanols **38** and CO_2 ; (b) plausible mechanism for the formation of **39**.



iodide to palladium(0), and then coordination of **A** to the allenic bond of alcohol **36** to give π -allylic palladium species **B**, which undergoes an intramolecular carbopalladation to produce intermediate **C**. Next, reaction of CO₂ with alkoxide group of **C** forms carbonate species **D**. Finally, an intramolecular cyclization of **D**, followed by a reductive elimination affords the observed products **37** (Scheme 16b).⁴⁷

Recently, the group of Zhang reported an efficient protocol for the synthesis of six-membered cyclic carbonates **39** from the reaction between commercially available 3-(pseudo)halo-1-propanols **38** and carbon dioxide through a Cs₂CO₃-catalyzed intermolecular ring closing strategy using mild reaction conditions. The corresponding cyclic carbonates were obtained in good to high yields (Scheme 17). Noteworthy, other bases such as K₂CO₃ and ^tBuOK were also found to promote the reaction; however, in lower yields. Under optimized conditions, the reaction also tolerated 2-(pseudo)halo-1-ethanols and gave corresponding five-membered cyclic carbonates in good to high yields, but the extension of the reaction to the synthesis of seven- and eight-membered rings was failed.⁴⁸

6. Conclusion

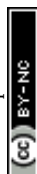
Carbon dioxide is a promising and sustainable carbon feedstock for producing value-added organic compounds. New catalytic protocols for efficient incorporation of CO₂ into acyclic and five-membered cyclic carbonates are continuously being reported. However, little progress has been made in the synthesis of six-membered cyclic carbonates in the presence of CO₂. As illustrated, synthesis of titled compounds using various substrates in the presence of CO₂ have gained a lot of interest in recent years as useful alternative procedures. Interestingly, some of the conversion of CO₂ covered in this mini-review could be easily achieved under ambient conditions. This results clearly show the potential application of these reactions in industry. Despite all these successes, the number of reported examples in this interesting field is limited. There is still further need to study the scope and limitations of this approach for the preparation of various six-membered cyclic carbonates.

Conflicts of interest

There are no conflicts to declare.

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