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Organocatalytic Transformation of Carbon Dioxide

Ruimao Hua and Sushmita Roy

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Abstract

Catalytic transformation of CO₂ into the value-added organic compounds is a very important and hot research topic in organic synthetic chemistry and green chemistry from the viewpoint of developing CO₂ as C resource. Organocatalytic reactions employing metal-free organic molecules as catalysts have received unprecedented attention in recent years, with the significant advantages of the catalysts being usually inexpensive and stable, and the reactions can be performed under air. This chapter summarizes and gives an overview of the recent advances in the organocatalytic transformation of CO₂ into cyclic carbonates, 2-oxazolidinones, carboxylic derivatives, as well as the synthesis of CO₂-adducts and their application as CO₂ carriers.

Keywords: carbon dioxide, CO₂-adduct, cyclic carbonates, organocatalysis, 2-oxazolidinones

1. Introduction

Carbon dioxide (CO₂) exhibits many good qualities as an ideal C resource in organic synthesis such as non-toxicity, natural abundance, and inexpensiveness. Therefore, a variety of efficient catalyst systems have been developed for the transformation of CO₂ into the useful and value-added organic compounds, even it is a kinetically and thermodynamically stable final product of all combustion processes of organic matters and some comprehensive reviews have been reported [1–3]. On the other hand, the organocatalytic reactions using simple, cheap, stable, and easily available organic compounds as catalysts for various organic transformations have been widely investigated in the past two decades [4–6] and have also played an important tool for catalytic activation of CO₂ and its transformation. In this chapter, we focus on summarizing the representative examples of the recent advancement on the organocatalytic transformation of

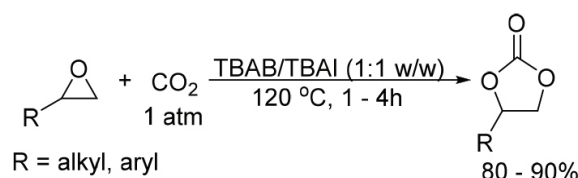
CO₂ into the different types of useful molecules, including cyclic carbonates, 2-oxazolidinones, ureas, and carbamates, as well as the CO₂-adducts and their application as CO₂ carriers.

2. Transformation of CO₂ into cyclic carbonates

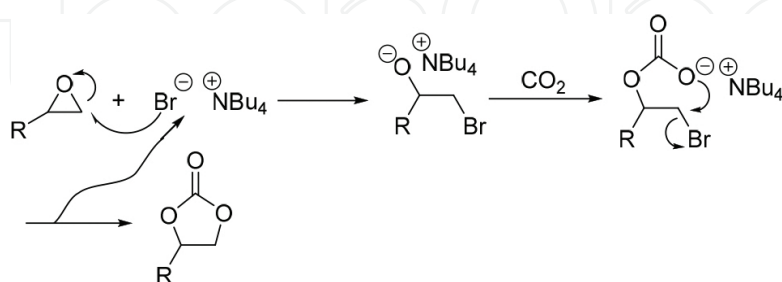
The coupling of CO₂ with epoxides is an atom-economic transformation for the synthesis of cyclic carbonates, which have high potential application as the aprotic polar solvents [7], electrolytes for lithium ion batteries [8], precursors for organic synthesis [9], and polymers [10].

Ionic liquids (ILs) have been well applied as the efficient organocatalysts in the coupling of CO₂ with terminal epoxides since it was first reported by Deng's group in 2001 using 1-*n*-butyl-3-methylimidazolium (BMIm) and *n*-butylpyridinium (BPy) salts as catalysts [11].

Caló [12] group reported a straightforward method for chemical fixation of CO₂ into terminal epoxides by simply dissolving epoxides in molten tetrabutylammonium bromide and iodide (TBAB and TBAI) as solvent under an atmospheric pressure of CO₂ (**Scheme 1**). The cyclic carbonates could be isolated by vacuum distillation or extraction with organic solvents, and the ionic liquid (IL) was insoluble allowing the recycling of the ammonium salt. In addition, polymerization sensitive epoxides also reacted very well to give the corresponding cyclic carbonates, and the reaction rate depended on the nucleophilicity of the halide ion as well as the structure of the cation. TBAI could be also used as the sole solvent, and at 60°C, the reactions gave the cyclic carbonates in the similar yields.



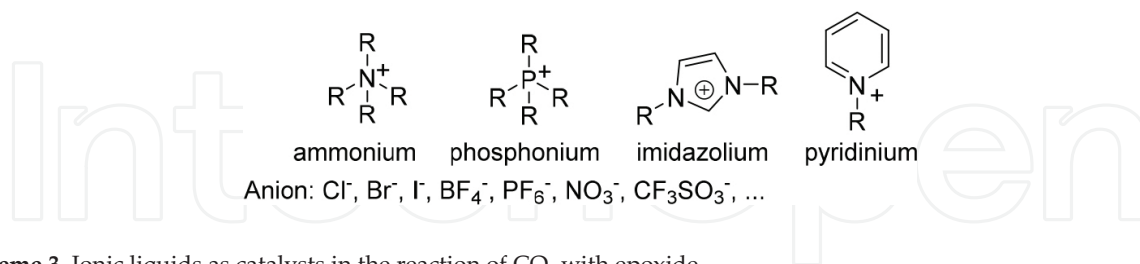
Scheme 1. Formation of cyclic carbonates in tetraalkylammonium salts.



Scheme 2. Plausible mechanism for cyclic carbonate formation in Bu₄NBr.

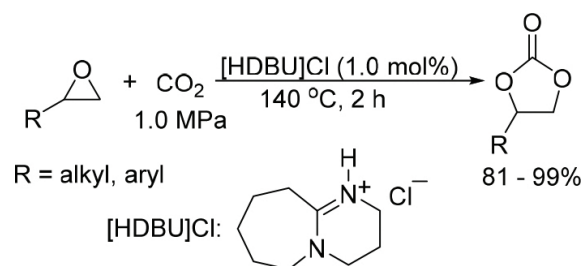
A plausible mechanism was proposed for the formation of cyclic carbonates including the steps of the ring opening of epoxide by a nucleophilic attack of bromide ion, and the reaction of CO₂ with the oxy anion species (**Scheme 2**).

Another IL such as quaternary ammonium-, phosphonium-, imidazolium-, or pyridinium-based cations with inorganic counter anions have been also used as the efficient catalysts in the synthesis of cyclic carbonate *via* the coupling of CO₂ with epoxides (**Scheme 3**) [13].



Scheme 3. Ionic liquids as catalysts in the reaction of CO₂ with epoxide.

He's group prepared a series of Lewis basic ILs and examined their catalytic activity in the synthesis of cyclic carbonate from CO₂ and epoxides under solvent-free conditions and established an efficient and recoverable catalyst system using [HDBU]Cl (1,8-diazabicyclo[5.4.0]undec-7-enium chloride) as organocatalyst (**Scheme 4**) [14]. The catalyst system also showed fair catalytic activity to internal cyclohexene oxide.

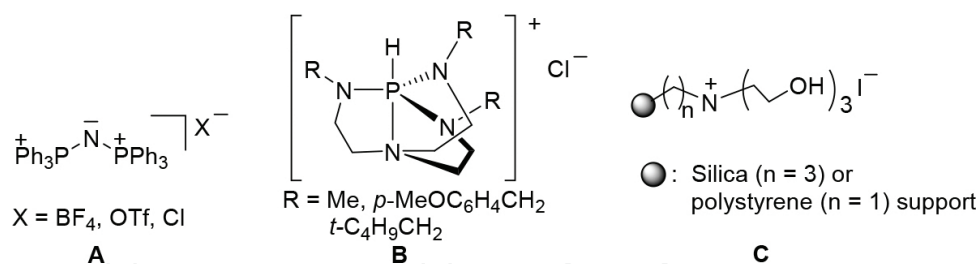


Scheme 4. Formation of cyclic carbonates catalyzed by recoverable [HDBU]Cl.

A further work of the same group designed and synthesized a series of polyethylene glycol (PEG)-functionalized basic ILs, and providing the alternative recoverable and high catalytic activity organocatalysts in the coupling of CO₂ with terminal and internal epoxides [15].

In addition, although PPN salts (**Scheme 5, A**) with weak nucleophilic anions such as PPN⁺BF₄⁻ and PPN⁺OTf⁻ were inactive for the coupling of CO₂ with epoxides, PPN⁺Cl⁻ salt was found to be a good organocatalyst for the coupling of CO₂ with neat epoxides without the use of organic solvents to afford cyclic carbonates [16].

Azaphosphatranes as tunable alternative to quaternary ammonium and/or phosphonium catalysts for the synthesis of cyclic carbonates from CO₂ and epoxides was also reported by Martinez and Dufaud's group (**Scheme 5, B**) [17]. In order to examine the nature of the nanospace of the molecular cavity to affect the stability and reactivity of azaphosphatranes as organocatalyst, the same groups further reported the synthesis of supramolecular azaphosphatranes having cavities of different size and shape, and their excellent catalytic activity in the synthesis of cyclic carbonates from CO₂ and epoxides [18].

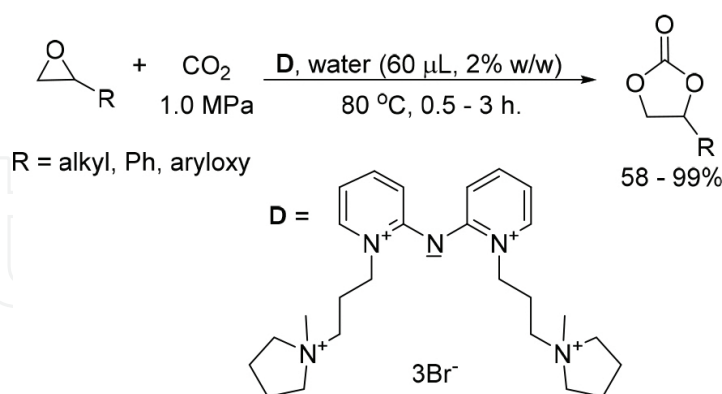


Scheme 5. Organocatalyst for the coupling of CO_2 with epoxides.

Werner's group synthesized a bifunctional ammonium salt covalently bound to a polystyrene or silica support, which showed efficient catalytic activity under solvent-free conditions for the synthesis of cyclic carbonates, developing an alternative recyclable and reusable organocatalyst for the coupling of CO_2 with epoxides (**Scheme 5, C**) [19].

In addition, in order to understand the mechanism of the coupling of CO_2 with epoxides catalyzed by quaternary ammonium salts, Zhang's group studied the mechanism by experimental and density functional theory (DFT). The detailed structural and energetic information about each step of the three elementary steps in the catalytic cycle were obtained, and the effects of the chain length and anion on the reaction mechanisms, as well as the outcomes were also reported [20].

Wong's group designed and synthesized a new IL (**D**), which showed high catalytic activity for the formation of cyclic carbonates under mild conditions in the presence of small amount of water (**Scheme 6**) [21]. The IL plays dual roles as an organocatalyst and the reaction medium. Moreover, IL was very robust under reaction conditions and could be recycled and reused constantly without showing any significant loss in its catalytic activity.

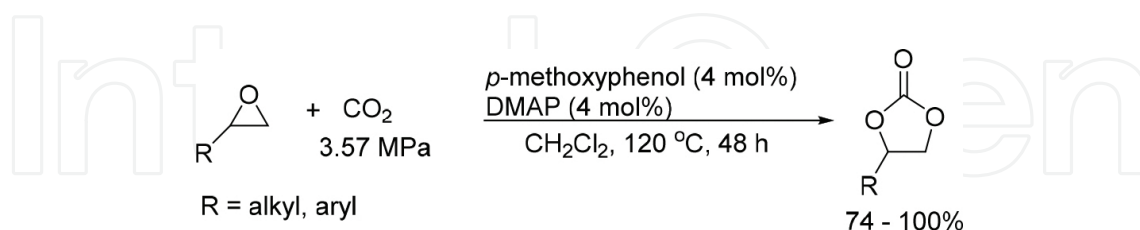


Scheme 6. Ionic liquid as the efficient organocatalyst and reaction medium in cyclic carbonate formation.

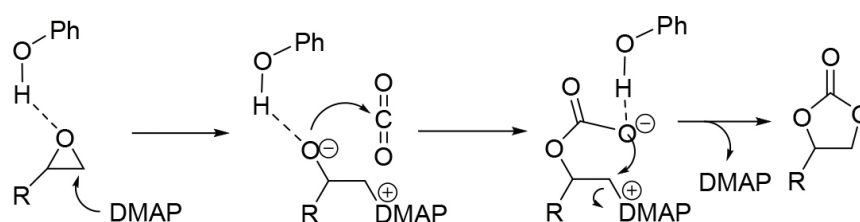
In recent years, the simple and cheap organic compounds have been also developed as the efficient organocatalysts in the activation of CO_2 and its transformation to cyclic carbonates.

Shi's group studied the catalytic activity of a combination of phenols with organic bases in the coupling of CO_2 with terminal epoxides and found that *p*-methoxyphenol with 4-dimethyl-

minopyridine (DMAP) was the best combination to give the cyclic carbonates the excellent yields (**Scheme 7**) [22]. A study of mechanism using *trans*-deuterioethylene oxide as the substrate disclosed that the formation of cyclic carbonate proceeded *via* the epoxy ring activated by phenol by hydrogen bonding and opened by amine (DMAP) and then reacting with CO₂ to give the corresponding cyclic carbonate (**Scheme 8**).



Scheme 7. Reaction of CO₂ with epoxide in the presence of *p*-methoxyphenol and DMAP.

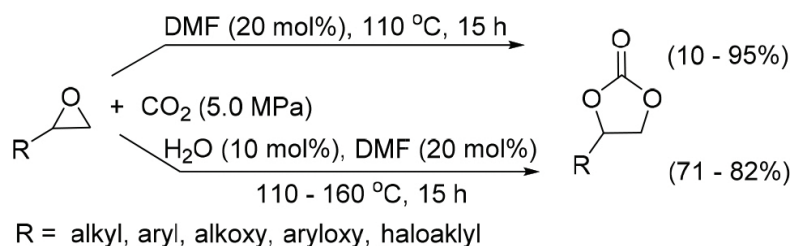


Scheme 8. Proposed mechanism for the formation of cyclic carbonates catalyzed by *p*-methoxyphenol and DMAP.

In addition, Maseras and Kleij's groups examined the catalytic activation of phenols/*n*-Bu₄NI in methyl ethyl ketone as solvent, and optimized pyrogallol/*n*-Bu₄NI was a powerful catalyst with ample substrate scope under very mild reaction conditions (25–45°C, P(CO₂) = 10 bar, 2–5 mol% catalyst) for the preparation of various cyclic carbonates from CO₂ and terminal epoxides [23]. Kleij's group further designed and synthesized the immobilized pyrogallol organocatalyst, developing an efficient and recyclable organocatalyst with a significant advantage of low reaction temperature (45°C) [24]. Furthermore, Kleij's group found that tannic acid, a naturally occurring plant polyphenol, was an efficient organocatalyst with the use of *n*-Bu₄NI as cocatalyst in the same transformation [25].

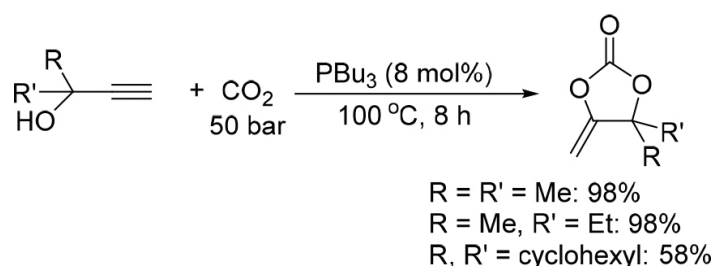
DMF-scCO₂ system was reported to be a good solvent system for the coupling of 1,2-epoxystyrene with CO₂ affording the corresponding cyclic carbonate [26]. A further investigation by Hua's group disclosed that under solvent-free conditions, the high yields of cyclic carbonates could be achieved by coupling of CO₂ with epoxides in the presence of catalytic amount of DMF [27], and in some cases, the catalytic activity of DMF could be significantly increased by the addition of catalytic amount of H₂O (**Scheme 9**).

Hua's group also investigated the catalytic activity of nitrogen-containing organic compounds, such as amines, anilines, amides, and pyridines in the formation of cyclic carbonates *via* the coupling of CO₂ with terminal epoxides, and confirmed that 2,2',2''-terpyridine was an excellent organocatalyst to catalyze such type of transformation [28].

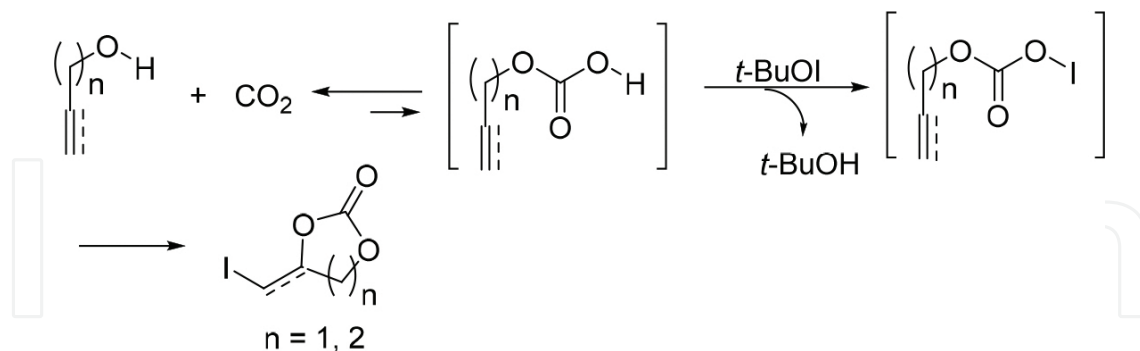


Scheme 9. DMF-catalyzed the formation of cyclic carbonates from CO₂ and epoxides.

On the other hand, the cycloaddition of propargyl alcohols with CO₂ is an efficient and alternative transformation for the formation of α -methylene cyclic carbonates, and Dixneuf's group first reported a PBu₃-catalyzed reaction of tertiary propargyl alcohols with CO₂ in an inert autoclave led to the high yield of the cyclic carbonates (**Scheme 10**) [29]. It was found that in the absence of other solvent, PBu₃ showed higher catalytic activity than PPh₃ and PCy₃.



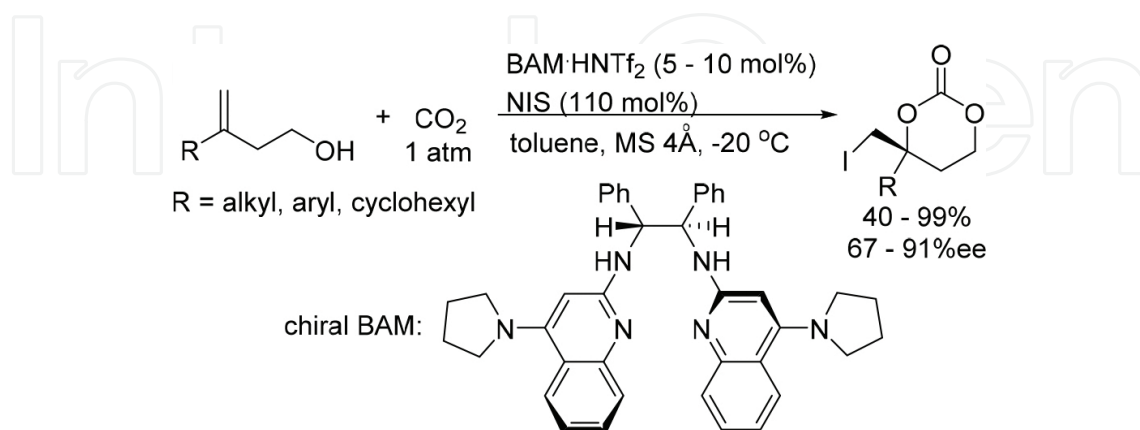
Scheme 10. PBu₃-catalyzed the reaction of tertiary propargyl alcohols with CO₂ affording α -methylene cyclic carbonates.



Scheme 11. The formation of iodo-substituted cyclic carbonates.

Minakata's group developed a strategy to offer an innovative approach to the fixation of CO₂ to a wide range of cyclic carbonates *via* the reaction of CO₂ with both olefinic and acetylenic alcohols including the steps of the formation of alkyl carbonic acid and its iodination, as well as the subsequent intramolecular cyclization (**Scheme 11**) [30]. The formation of iodo-substituted cyclic carbonates results in high potential application of the presented strategy in organic synthesis.

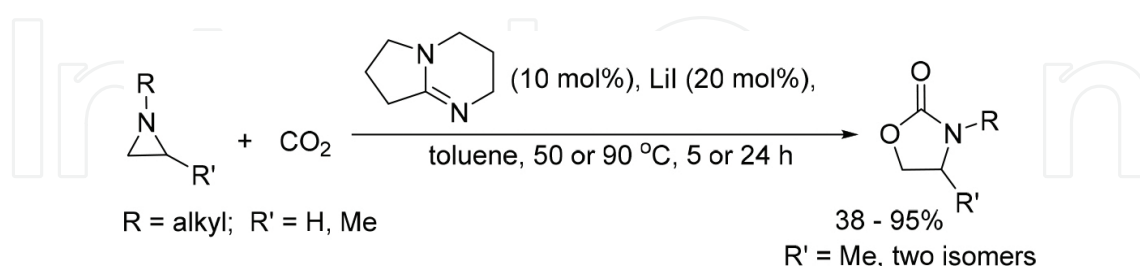
Johnston's group also reported a three component reaction of CO₂, homoallylic alcohol and NIS (NIS = *N*-iodosuccinimide, an electrophilic source of iodine) using a chiral BAM catalyst having dual Brønsted acid/base role that presents hydrogen-bond donor and acceptor functionality to activate and adjust substrates in an enantioselective reaction, and cyclic carbonates were obtained enantioselectively (**Scheme 12**) [31].



Scheme 12. Cyclic carbonates from homoallylic alcohol, CO₂ and an electrophilic source of iodine.

3. Transformation of CO₂ into 2-oxazolidinones

Substituted 2-oxazolidinones are one of the important five-membered heterocyclic compounds, which not only show interesting biological and physiological activities but also have been applied as starting materials in the synthesis of other functional compounds. The coupling of CO₂ with aziridine, CO₂ with propargylamine, as well as the three-component cycloaddition of CO₂, propargyl alcohol, and primary amine is the most interesting and promising synthetic methods.

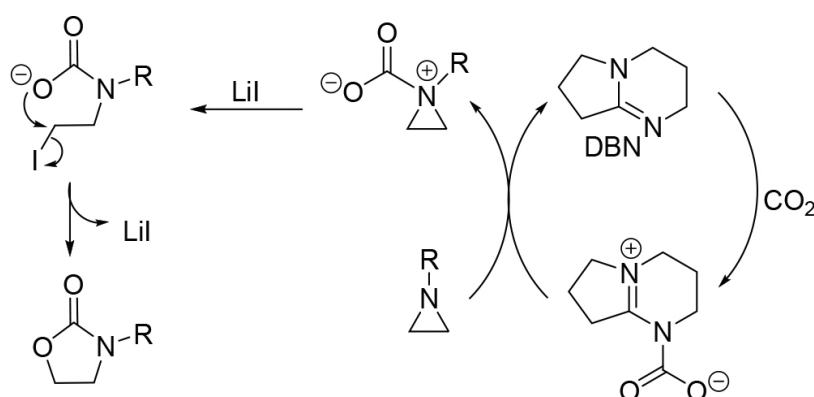


Scheme 13. Synthesis of 2-oxazolidinones from CO₂ and aziridine catalyzed by DBN.

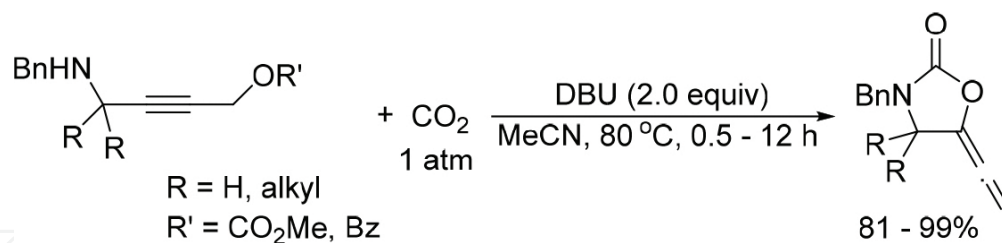
He's group designed and synthesized a series of polyethylene glycol (PEG)-functionalized ionic liquids as recyclable and efficient organocatalysts for selective synthesis of 5-substituted-2-oxazolidinones from the coupling of CO₂ and aziridines. It was found that PEG₆₀₀₀(NBu₃Br)₂ (PEG MW6000) [32] and BrDBN-PEG₁₅₀-DBNBr (DBN: 1,5-diazabicyclo[4.3.0]non-5-ene; PEG MW150) [33] were the efficient catalyst not only affording the

expected 5-substituted-2-oxazolidinones in good yields, but also showing excellent regioselectivities. The same group also developed a proline-catalyzed synthesis of 5-aryl-2-oxazolidinones from CO₂ and aziridines under solvent-free conditions [34].

Liu's group developed an efficient catalytic system using DBN as organocatalyst and LiI as an additive under atmospheric pressure of CO₂ in toluene to catalyze the coupling of CO₂ with aziridines giving 2-oxazolidinones (**Scheme 13**) [35]. The procedure was tolerated by a number of *N*-alkyl aziridines bearing various functional groups in alkyl terminal position, but *N*-tosyl aziridines did not undergo the coupling reaction probably due to the less nucleophilic activity of the nitrogen. In addition, the formation of the DBN-CO₂ was proposed to be the intermediate of the catalytic cycle (**Scheme 14**).



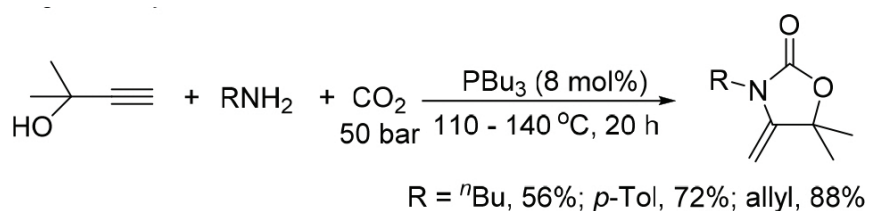
Scheme 14. Proposed mechanism in the synthesis of 2-oxazolidinones from CO₂ and aziridines catalyzed by DBN.



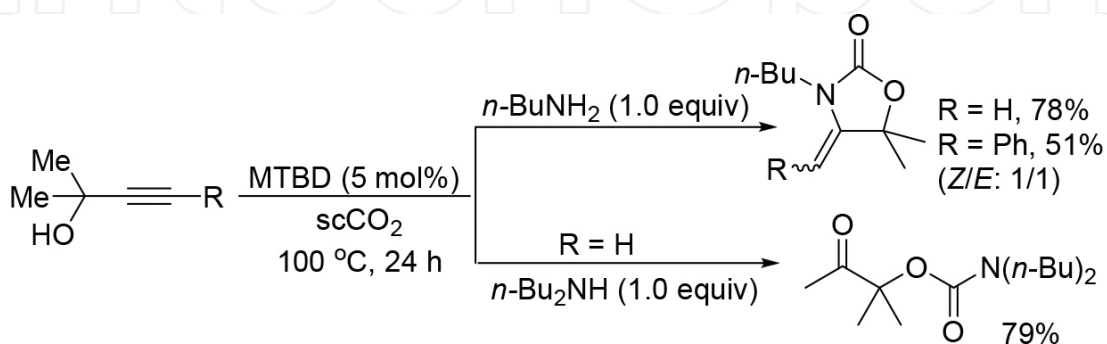
Scheme 15. DBU-mediated synthesis of substituted 5-vinylideneoxazolidin-2-ones.

Yoshida and Ihara's groups investigated the reaction of 4-(benzylamino)-2-butynyl carbonates and benzoates with an atmospheric pressure of CO₂ in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), developing a DBU-mediated synthesis of substituted 5-vinylideneoxazolidin-2-ones, which are attractive and important compounds in both medicinal and synthetic organic chemistry (**Scheme 15**) [36].

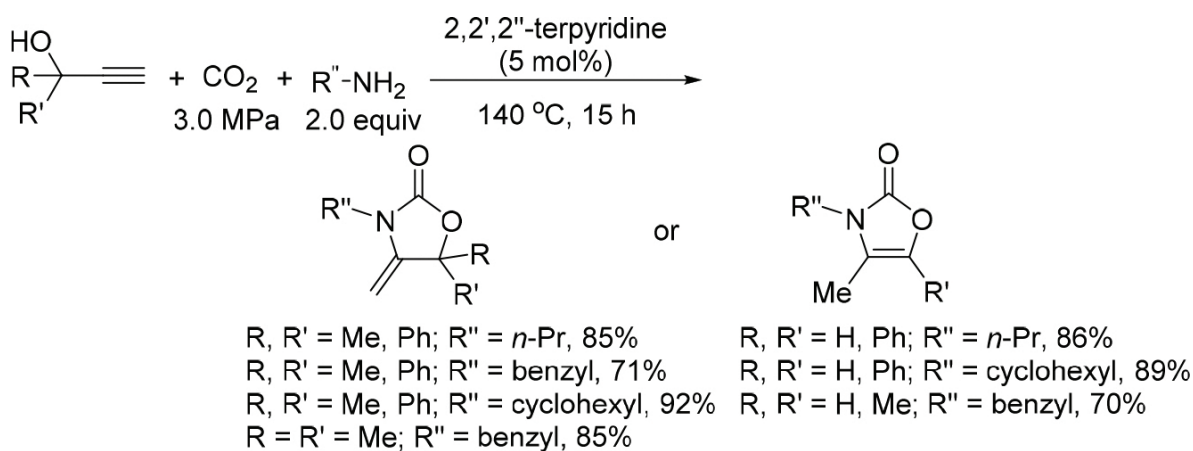
The three-component cycloaddition of CO₂, propargyl alcohol and primary amine catalyzed by organocatalyst affording 4-methylene-2-oxazolidinones was first reported by Dixbeuf's group with the use of simple and cheap PBU₃ as catalyst and use of an excess amount of tertiary propargylic alcohols (**Scheme 16**) [37].



Scheme 16. PBu₃-catalyzed three-component cycloaddition of CO₂, propargyl alcohol and primary amine affording 4-methylene-2-oxazolidinones.

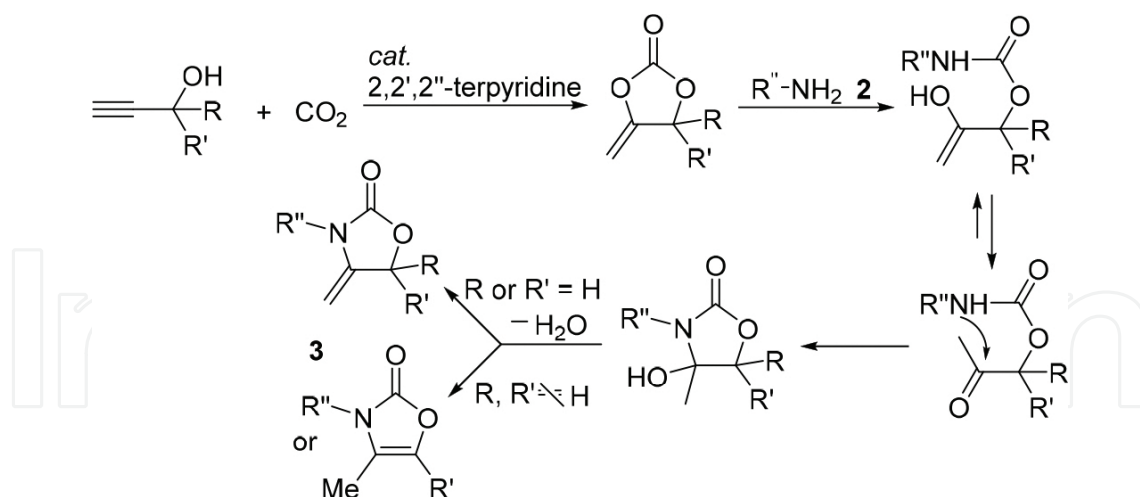


Scheme 17. Reaction of propargyl alcohol with scCO₂ in the presence of MTBD.



Scheme 18. Synthesis of 4-methylene-2-oxazolidinones or 2(3H)-oxazolones catalyzed by 2,2',2''-terpyridine.

Costa's group studied the synthesis of cyclic carbonates or carbamates and oxalkyl carbonates or carbamates *via* the direct incorporation of CO₂ into propargyl alcohol using either scCO₂ as solvent and reagent or gaseous CO₂ in MeCN as the solvent in the presence of a variety of organic bases. It was found that bicyclic guanidines, such as MTBD (1,3,4,6,7,8-hexaydro-1-methyl-2H-pyrimido[1,2-*a*]pyrimidine), TBD (2,3,4,6,7,8-hexaydro-1H-pyrimido [1,2-*a*]pyrimidine), and TBD-pol (1,3,4,6,7,8-hexaydro-2H-pyrimido [1,2-*a*]pyrimidine supported on polystyrene), could effectively catalyzed CO₂ transformation to the different carbonyl compounds depending upon the use of external nucleophiles [38]. As shown in **Scheme 17**, in



Scheme 19. Proposed mechanism for the formation of 4-methylene-2-oxazolidinones and 2(3*H*)-oxazolones.

the presence of MTBD, the reactions of propargyl alcohols with primary and secondary amines selectively afforded α -methyleneoxazolidinones and acyclic carbamates in good yields, respectively.

Hua's group also investigated the three-component cycloaddition of CO_2 , propargyl alcohol and primary amine in the presence of pyridine and its derivatives as organocatalysts under solvent-free conditions, and 2,2',2''-Terpyridine was found to be the efficient organocatalyst to afford 4-methylene-2-oxazolidinones or 2(3*H*)-oxazolones in good to high yields depending on the structures of propargyl alcohols (**Scheme 18**). A proposed mechanism for the formation of 4-methylene-2-oxazolidinones and 2(3*H*)-oxazolones is depicted in **Scheme 19**, it includes the formation of α -methylene cyclic carbonate as intermediate, and its nucleophilic addition reaction with primary amine to give *N*-alkylcarbamate, subsequent cyclization by intramolecular nucleophilic addition reaction and dehydration reaction affording 4-methylene-2-oxazolidinones or 2(3*H*)-oxazolones, depending upon the substituents *R* and *R'*.

In addition, 2,2',2''-terpyridine also showed high catalytic activity in the coupling of CO_2 with aziridines bearing either electron-donating or electron-withdrawing *N*-substituents to give substituted 2-oxazolidinones in high yields. Therefore, 2,2',2''-terpyridine was applied as an efficient organocatalyst in the transformation of CO_2 into not only cyclic carbonates [28], but also 2-oxazolidinones and 2(3*H*)-oxazolones [39].

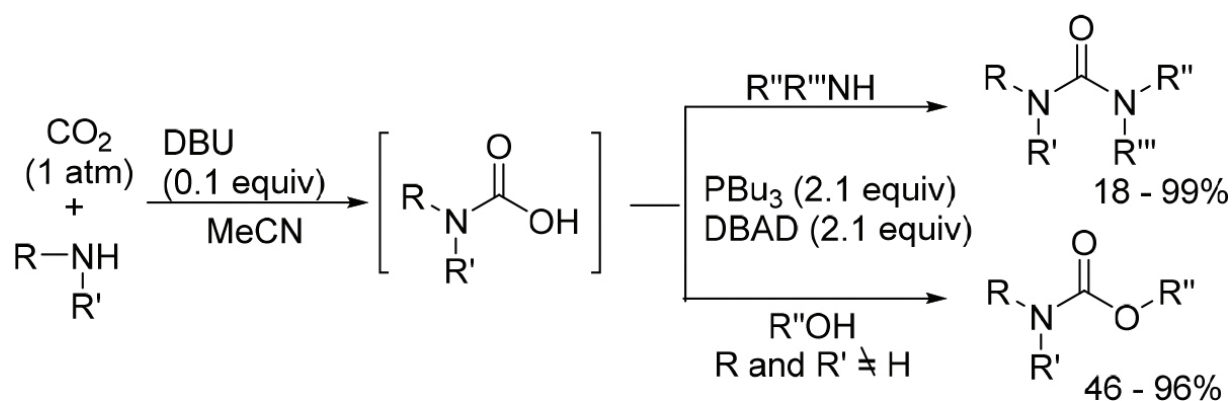
In addition, ILs were also reported to be the effective promoter and reaction media for the synthesis of 4-methylene-2-oxazolidinones from CO_2 , propargyl alcohol, and amines with high yields [40].

4. Transformation of CO_2 into carboxylic derivatives

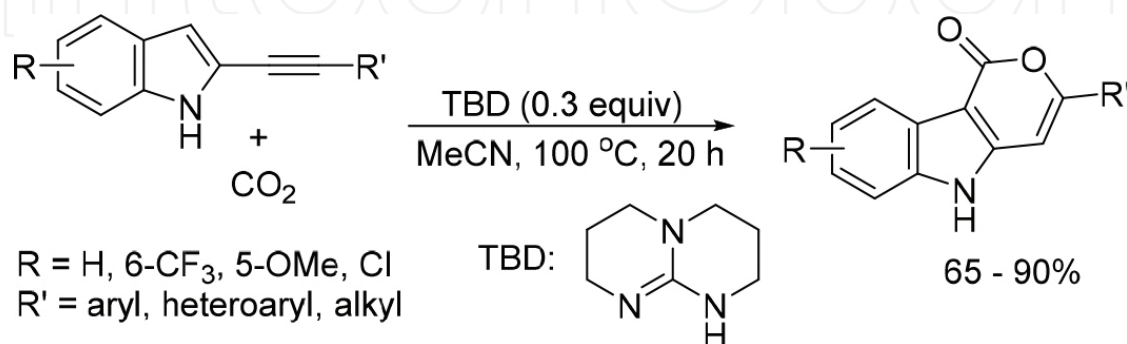
CO_2 is one of the good candidates in the synthesis of carboxylic derivatives. Nitrogen-containing organic bases mediated the formation of diarylureas *via* the reaction of CO_2 with

aromatic amines was a well-known procedure [41–42]. It has been also known that carbamic acids derived from the reaction of amines with CO₂ gas can be transferred into isocyanates, and then ureas and carbamates *via* the further reactions with amines or alcohols. Peterson's group reported the parallel synthesis of ureas and carbamates from CO₂ and amines catalyzed by DBU and in the presence of PBu₃/DBAD (Mitsunobu reagent [43]; DBAD: di-*t*-butylazodicarboxylate) (Scheme 20) [44]. It was proposed that carbamic acids derived from primary amines reacted with Mitsunobu reagent to generate isocyanates in situ, which were condensed with primary and secondary amines to afford the expected unsymmetrical di- and trisubstituted ureas. Similarly, carbamic acids from secondary amines reacted with alcohols activated with Mitsunobu reagents to form carbamates *via* an S_N2 mechanism.

Skrydstrup's group investigated the CO₂ trapping with 2-alkynyl indoles in the presence of various organic bases and developed an efficient TBD-catalyzed the cycloaddition of CO₂ with a variety of substituted 2-alkynyl indoles to afford tricyclic indole-containing ring compounds, good results were obtained with aromatic, heteroaromatic, and aliphatic 2-alkynyl indoles in terms of both yields and selectivities (Scheme 21) [45]. The new methodology developed a procedure for the formation of C-C bond between CO₂ and an indole derivative catalyzed by an organocatalyst.



Scheme 20. Parallel synthesis of urea and carbamate from CO₂ and amine via carbamic acid.

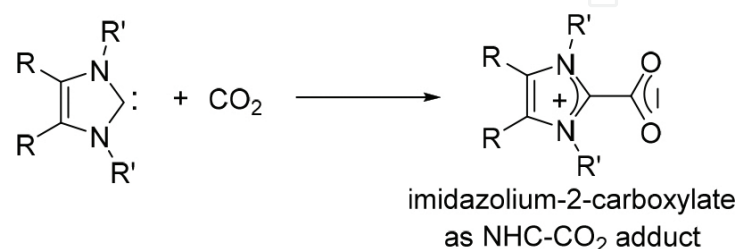


Scheme 21. TBD-catalyzed cycloaddition of CO₂ with 2-alkynyl indoles.

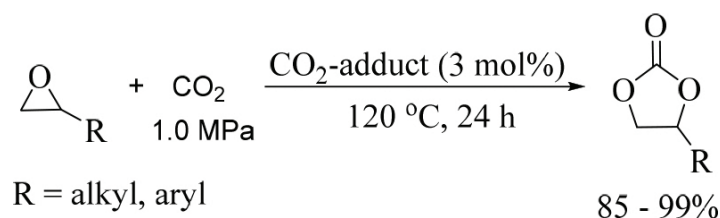
5. CO₂-adduct and its use as precatalyst in CO₂ transformation

CO₂ is a typical electrophilic reagent, and the synthesis and application of its adduct with nucleophiles have been considered to be an efficient way for CO₂ capture, activation, and further transformation.

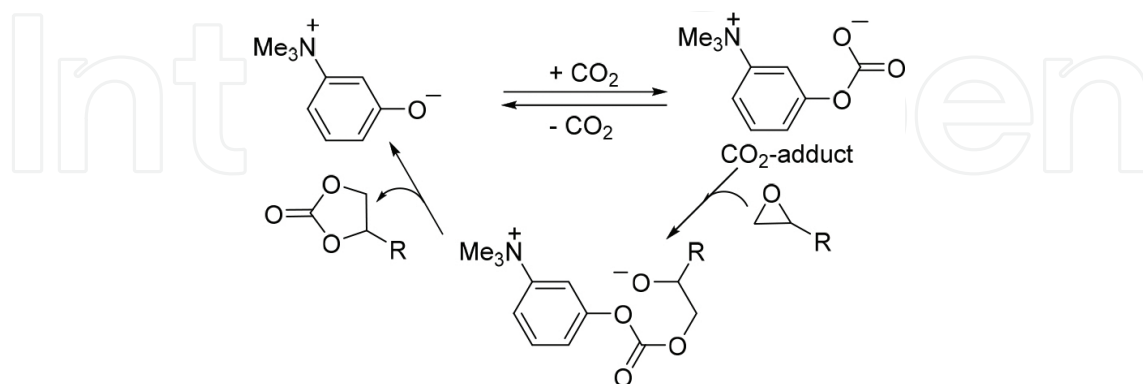
DBU-CO₂ adduct could be prepared and isolated as a white powder in good yield by the reaction of DBU with CO₂ in anhydrous acetonitrile at 5°C and was first used as the efficient carrier of CO₂ in the synthesis of *N*-alkyl carbamates by a transcarboxylation of amines and subsequent *O*-alkylation using ethyl iodide [46].



Scheme 22. Formation of NHC-CO₂ adduct.



Scheme 23. Formation of cyclic carbonates from CO₂ and epoxide catalyzed by CO₂-adduct.



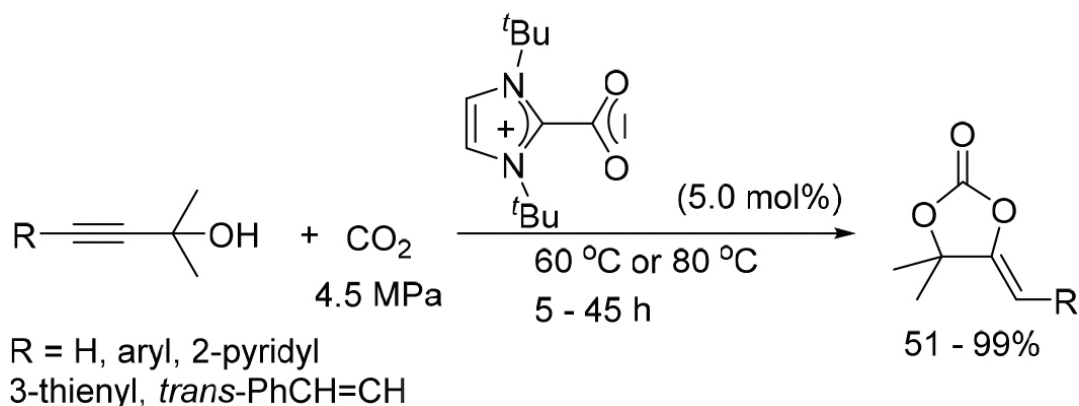
Scheme 24. Betaine-CO₂ adduct as key intermediate in the formation of cyclic carbonates.

On the other hand, unsaturated NHCs with the unique property of the carbon atom having strong basicity, stabilized by the electron-donating heteroatoms on either side, have been

applied as versatile ligands in transition metal complexes and organocatalysts [47]. NHCs have been found to react easily with CO₂ by its nucleophilic addition to C=O bond as the key step, resulting in the formation of carboxylates, a NHC-CO₂ adduct proposed as carriers of NHC as well as CO₂ (**Scheme 22**) [48–50].

Sakai's group designed and synthesized bifunctional organocatalysts bearing an ammonium betaine framework, which showed high catalytic activation of CO₂, and catalyze the coupling of CO₂ with terminal epoxides affording cyclic carbonates in good yields (**Scheme 23**) [51]. Among them, 3-(trimethylammonio)phenolate was found to be one of the most active organocatalysts, and the formation of betaine-CO₂ adduct was demonstrated to be the key intermediate (**Scheme 24**).

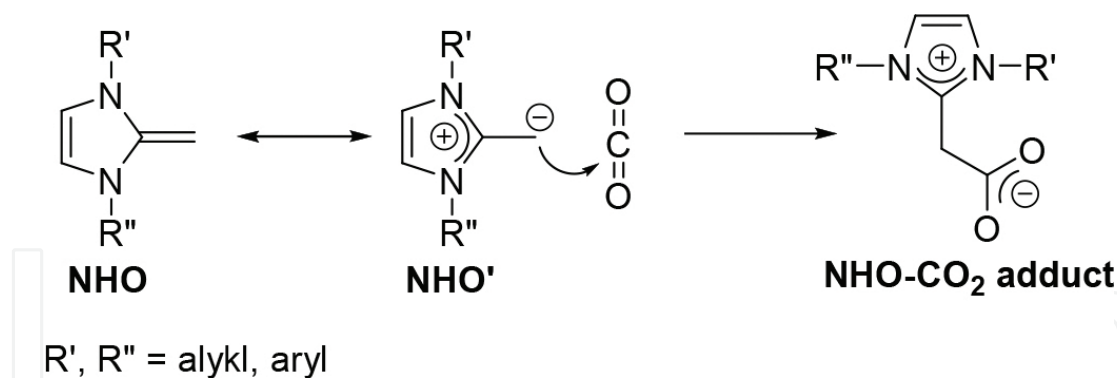
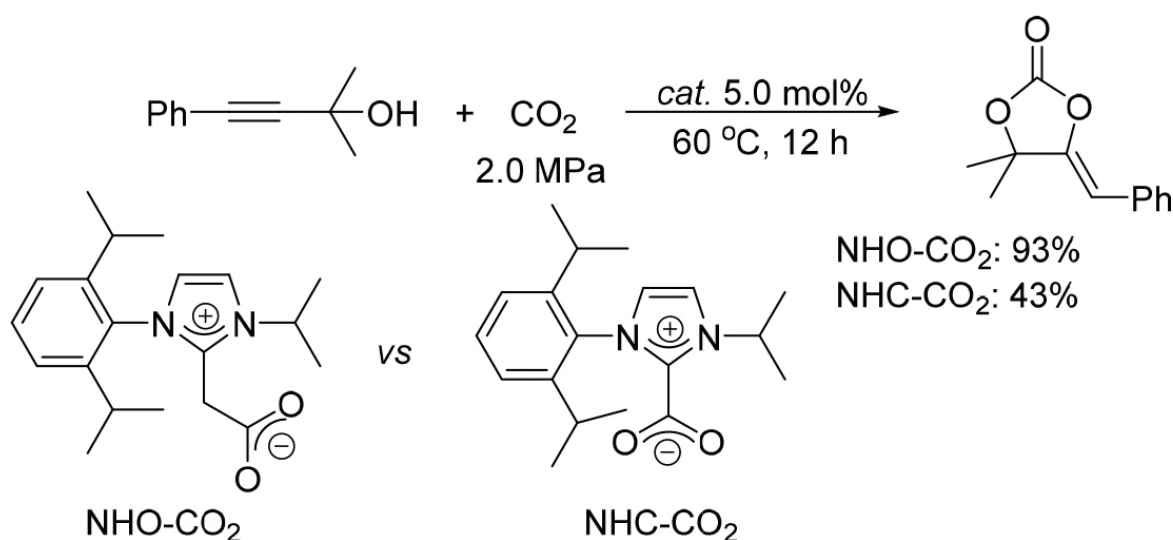
Moreover, several thermally stable CO₂ adducts of *N*-heterocyclic carbenes (NHC-CO₂) from the reaction of CO₂ with NHCs were found to be the efficient organocatalysts in the coupling of CO₂ with epoxides [52].



Scheme 25. Formation of 4-methylene cyclic carbonates catalyzed by NHC-CO₂ adduct.

In addition, Ikariya's group synthesized several 1,3-dialkylimidazolium-2-carboxylates (NHC-CO₂ adduct) and investigated their catalytic activity in the cycloaddition reaction of CO₂ with propargyl alcohols affording 4-methylene cyclic carbonates (**Scheme 25**) [53]. 1,3-di-*t*-butylimidazolium-2-carboxylate showed high catalytic activity under solvent-free conditions for the formation of the desired cyclic carbonates, and the reaction catalyst tolerated substrates bearing heterocycles such as pyridine and thiophene. The substrate having an olefinic group at the acetylenic terminus also provided the desired 5-exo-dig cyclization product in good yield. In addition, the C=C double bond at 4-position was found to have a *Z* configuration as determined by NMR spectroscopy, indicating that the addition to the alkynes proceeded predominantly in a *trans* fashion. Moreover, the catalyst was also found to be successful in the cyclic carbonate synthesis *via* the coupling of CO₂ with epoxides.

1-*n*-butyl-3-methylimidazolium-2-carboxylate was also applied as organocatalyst in the synthesis of glycerol carbonate *via* transesterification of glycerol with dimethyl carbonate (DMC) [54].

Scheme 26. Formation of NHC-CO₂ adduct.Scheme 27. Formation of 4-methylene cyclic carbonates catalyzed by NHC-CO₂ and NHC-CO₂ adducts.

N-heterocyclic olefin (NHO), shown in **Scheme 26**, is considered to be advantageous to stabilize a positive charge due to the aromatization of the heterocyclic ring resulting in the terminal carbon atom of the olefins more electronegative (NHO'). Therefore, NHO was considered as potent nucleophile for CO₂ capture, activation, and further transformation. Lu's group first synthesized a variety of NHO-CO₂ adducts and studied their catalytic activity in the reaction of CO₂ with propargyl alcohols giving 4-methylene cyclic carbonates (**Scheme 27**) [55]. It was found that NHO-CO₂ not only showed high catalytic activity for the transformation, but also showed higher catalytic activity compared to the corresponding NHC-CO₂ adducts at the same reaction conditions. The higher activity of NHO-CO₂ adduct was tentatively attributed to its low stability for easily releasing the CO₂ moiety and/or the desired product in a possible rate limiting step in the catalytic cycle.

The same group also reported the synthesis of various CO₂, COS, and CS₂ adducts of NHO, and these adducts were found to be efficient in catalyzing the cycloaddition reaction of CO₂

with epoxides to selectively afford the corresponding cyclic carbonates. Among them, NHO-CO₂ adducts were found to be more active [56]. Furthermore, a variety of CO₂ adducts of phosphorus ylides were prepared by the same group, and they were demonstrated to be the highly active organocatalysts for CO₂ transformation under mild conditions to cyclic carbonates, oxazolidinone, N-methylated, and N-formylated amines [57].

6. Conclusion

The use of CO₂ as a C starting material for the synthesis of useful and value-added organic compounds is an important and challenge research topic in the academic and industrial interest. The representative examples summarized in this chapter suggest that the simple, easily available, oxygen- and moisture-tolerated organocatalysts have played an important role in developing the promising and practical catalysis for the transformation of CO₂ to various organic compounds. It seems reasonable to expect that the organocatalyzed CO₂ transformation to much more different types of functional organic compounds will be greatly developed with the inspiration of the reported innovative progress. For example, Cantat's group recently developed the novel and interesting organocatalyst systems for the transformation of CO₂ to methylene in the synthesis of aminal derivatives, and CO₂ as CO source in the formylation of amines using hydrosilanes as reductants catalyzed by nitrogen-containing organic bases [58–59]. The simple accessibility of CO₂ and the vast range of possibilities to introduce various functional groups are some of the attractive features of CO₂ transformations.

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